THERMAL DIFFUSION IN SOME AQUEOUS SOLUTIONS

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by

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C O N T E N T S

INTRODUCTION

1. GENERAL

A temperature gradient applied to a mixture of gases or of liquids results in a gradient in the concentration of each component along that temperature gradient. This phenomenon is known as Thermal Diffusion. A great deal of experimental work has been done with gases but much less has been done with liquids. The theory of the process also has been the subject of much investigation in the case of gases, but again on the theoretical side less attention has been given to liquids. There is in fact much need for more experimental work in the case of liquids in order to study the effect of varying the various parameters which control the separation, with a view to further development of the theory.

There are two distinct ways in which thermal diffusion experiments may be carried out:-

(i) without convection, (ii) with convection.

The former are the easier to treat theoretically but the actual separations obtained are much smaller than in the latter case. Experiments of both kinds have been carried out with liquids and with gases, and it is proposed to give a short summary of this work. It will be convenient to treat this under four distinct headings /

headings:-

(a) Thermal diffusion in Liquids without convection.

(b) Thermal diffusion in Gases without convection.

(c) Thermal diffusion in Gases with convection.

(d) Thermal diffusion in Liquids with convection.

This is the order in which the phenomena were observed experimentally.

(a) Thermal Diffusion in Liquids without convection.

(often called The "Soret" Effect)

As far as is known the first experiments which were carried out on thermal diffusion in Liquids were those of Ludwig.[1] He joined together the necks of two retorts and filled the resulting vessel which was essentially an inverted U-tube, with a solution of sodium sulphate. The bulb of one of the retorts was placed in boiling water and the other in melting ice, and after two days a crust of crystals appeared in the cold bulb. After eight days the solution was decanted from these crystals and analysed, and the solution from the hot bulb was also analysed, when it was found that there was 0.44% more of the salt in the solution in the cold bulb than in the hot. This greater concentration in the region of lower temperature is thus the first demonstration of the effect. Ludwig also believed that the solid which separated was due directly to the effect /

effect. But it can readily be shown that this is not so; the solid appears on account of the smaller solubility of sodium sulphate at the lower temperature. This observation of Ludwig is misleading for it gives the impression that thermal diffusion in Liquids is a large effect, which is not the case. The effect is small, the period of time required to reach equilibrium is large and accidental convective mixing may entirely obliterate any separation.

This experiment was apparently the only one carried out by Ludwig but Soret[2], without knowledge of this work, deliberately set out to investigate the effect of a temperature gradient on solutions. In his first experiments with sodium chloride and potassium nitrate he used both U-tubes (not inverted) and straight vertical tubes, heated to 80°C. at the top and water-cooled at the foot. Straight tubes were found to give larger and more reproducible differences in concentration than U-tubes, and in all his subsequent work he used straight tubes. Such an arrangement tends to minimise convection for the solution in the cooler region always becomes more dense in the course of the experiment. In his earlier experiments Soret allowed the tubes to be exposed to the gradient for 23 days; in the later experiments for 56 days. Comparison of the results showed that equilibrium was not established in 23 days. There is no way of knowing whether it /

it was established in 56 days either, for no determinations of any other duration are recorded. Soret examined the chlorides of Li, Na, and K and found that the effect increased from Li to K. He also examined copper sulphate solutions and got a very large effect. The effect has been described as erratic and compared, in that connection, with solubility. There still is no method of knowing in advance whether a given salt will have a large or a small Soret effect. Berchem[3] and later Arrhenius[4] repeated and extended the determinations of Soret in their original form, but all subsequent workers have devoted their attention to the alteration of the experimental conditions so that equilibrium may be reached in a much shorter time. Examples are given by the work of Wereide[5], Eilert[6] and Chipman.[7] The last in particular used smaller vessels and a smaller temperature gradient (10°C). Further, by the use of a conductivity method, he was able to follow the process as it proceeded, without disturbing the solutions. He also attempted to diffuse solutions of non-electrolytes but obtained no result. Tanner[8] reduced the size of the cell still further but used a slightly larger gradient (24°C). He also used a method of analysis which did not disturb the solution (based on refractive index) and studied more concentrated solutions. Amongst many other solutes he tried sucrose and glycerol and got small but quite definite results.

results. The separations obtained with non-electrolytes are about one tenth of those for electrolytes.

Chipman, Tanner and many other investigators have collected a mass of experimental data on the Soret effects of many salts, acids and bases, but there has been little success in correlating the results. In many cases there appears to be an optimum concentration at which a maximum separation is obtained. For hydrochloric acid, for example, it occurs at about Normal. Van t'Hoff[9] attempted to give a theory of the process on the assumption that the change in concentration is such as to make the osmotic pressure in all parts of the system the same but this was shown to be erroneous by Arrhenius and Abegg.[10] A recent review of all the suggested theories by Hartley[11] demonstrates that no simple thermodynamical method can hope to explain the effect and a more satisfactory approach seems to be that of Eastman[12] which is rather complex. It must in fact be admitted that the Soret effect is not yet completely understood.

(b) Thermal Diffusion in Gases without convection

(often called "Simple" thermal diffusion)

The historical development of thermal diffusion in Gases took quite a different course from that in Liquids. Enskog[13] in 1911 first showed on theoretical grounds /

grounds that the effect should exist and this conclusion was also reached by Chapman[14] independently soon afterwards. The first experiments were carried out by Dootson[15] under the direction of Chapman with the definite object of demonstrating the effect experimentally. In the first experiment two 100 c.c. glass bulbs were arranged vertically and connected by a 5 m.m. internal diameter glass tube and stopcock. The upper bulb was maintained at 230°C in a sand bath and the lower one was cooled by water at 10°C. The mixture used was equal parts of carbon dioxide and hydrogen by volume, since the theory predicted a large separation for these gases and in these proportions. After four hours the stopcock was closed and the contents of each bulb analysed, when a small but definite separation was found, which was about one half of that predicted by the theory. This order of agreement between the theoretical and experimental results is usual in this work.

The theory assumes that the molecules behave like rigid elastic spheres and the deviation from the theoretical value is a rough measure of the "softness" of molecular collisions; for molecules whose law of interaction is that of the inverse fifth power of the distance (Maxwellian molecules - "very soft") the effect should vanish. Speaking generally the theory predicts that the effect should exist whenever the masses /

masses or the diameters of the molecules of the gases used are different and it should be greater if the differences are greater. Also it should be a maximum for a mixture of 50% by volume of the gases. In the course of the development of the theory Chapman[16] pointed out that the method should be useful for the separation of gases of the same molecular weight but of different diameters such as carbon dioxide and nitrous oxide and also for the separation of isotopes which have the same diameter and differ only in mass. However it is only recently that these expectations have been realised, and not entirely as Chapman anticipated.

The experiments of Dootson were intended solely as qualitative confirmation of the theory and are mainly of historical interest, but since then technique has continuously improved and the measurements can now be made with considerable precision - in most cases without disturbing the system. Ibbs[17] and his collaborators have employed for this purpose the "katharometer," devised by Shakespear,[18] which uses the thermal conductivity of the gas mixture as a measure of its composition and have produced very complete data for binary mixtures of the inert gases. For this work they used temperatures as low as -190°C for the cold side. Blüh, Blüh and Puschner[19] have used the refractive index of the gas measured interferometrically with considerable success, especially for the study of mixtures containing carbon /

carbon dioxide which appear to behave rather anomalously. Harrison[20] used the gamma-ray activity of radon to study the behaviour of its binary mixtures with helium and hydrogen; exceedingly small amounts of radon were present in each case. It is interesting to note that despite the greater mass difference, greater separations were obtained with helium. This is quite usual when mixtures containing hydrogen and helium are compared in this way and is taken to indicate the extreme "hardness" of the helium molecule. More recently A. O. Nier[21] has used a mass spectrograph to examine thermal diffusion effects in a single gas containing two isotopes such as methane $^{12}CH_4$ & $^{13}CH_4$. For this purpose he has varied the technique slightly making use of the observation of Ibbs, Grew & Hirst[17] that the separation is independent of the pressure. The two-bulb system is filled with the gas and exposed to the gradient. Then the hot bulb is isolated and evacuated and the contents of the cold bulb allowed to expand into it, when the new mixture is exposed to the gradient and the whole cycle repeated. This is done twelve times and then the isotope abundances determined, when a definite separation is observed. This technique has since been successfully applied to neon, argon[22] and ammonia.[23] Before leaving the practical side it should be mentioned that Ibbs[24] has used two continuous flow methods successfully to demonstrate the effect. *See also ref. 76.*

Whereas /

Whereas the theory has a sound mathematical basis (Chapman & Cowling[25]) the physical principles involved cannot be easily appreciated by examination of the theory. A simplified theory which endeavours to remedy this defect has been given by Gillespie[26]. The equations he obtains are quite similar to those of Chapman and fit the results equally well in many cases. Fürth[27] has succeeded in deriving Chapman's equations in a simple manner using the method of mean free paths. Frankel[28] has given an explanation for the existence of the effect by an argument based on dimensions.

In concluding this section it should be noted that like the Soret Effect, this effect is small.

(c) Thermal Diffusion in Gases with convection

In 1938 Clusius & Dickel[29] announced that they had discovered a new technique for carrying out Thermal Diffusion experiments. In this apparatus of new design, convection, which can obliterate separation, is used to multiply the effect. In "simple" thermal diffusion experiments it is usual, as indicated above, to arrange that the hot side is placed above the cold to eliminate convection, an arrangement which can be represented diagramatically as in Fig 1 (a).

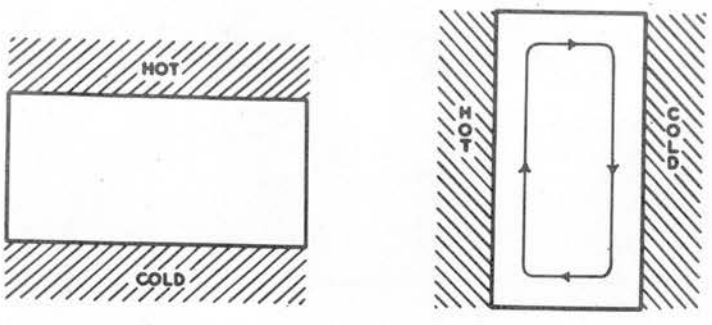


FIG. 1

If now this arrangement be rotated through 90° in the plane of the paper the new arrangement will be as shown in Fig 1 (b). Conditions are then quite different; for the gas at the hot side by virtue of its high temperature will be of lower density than the gas at the cold side and accordingly a convection current will be set up as shown by the arrows. This current would be set up even in a pure gas and is quite independent of thermal diffusion. But in the case of a gas mixture, despite its mass movement, the temperature gradient will still exert an effect and as a result there will tend to be, in the general case, at any instant, at a given level, slightly more of the heavier molecules at the cold side and slightly more of the lighter molecules at the hot side. Consequently the ascending current of gas will be richer in the lighter molecules and the descending current richer in the heavier ones, and in due course the heavier molecules will preponderate at the foot and the lighter ones at the /

the top. For although the convection current will tend to carry light molecules down the cell again these light molecules will diffuse back to the hot side, before they get very far down, and thus rise to the top again, so that for practical purposes a state is soon reached in which the light molecules circulate around the upper portion of the cell while the heavy molecules circulate around the lower portion. This method of multiplying the separation due to thermal diffusion works very well, and is limited not by the magnitude of the thermal diffusion effect, but by the tendency of the convection current and ordinary ("concentration") diffusion to remix the gases.

In their first experiment Clusius & Dickel[30] used a mixture of carbon dioxide and hydrogen to get a large effect just as Chapman and Dootson had done under similar circumstances. The mixture at atmospheric pressure was placed in a 1 cm. (internal) diameter glass tube of length 93 cm., which was externally cooled by a water jacket. Down the axis of the tube there was a nichrome wire of 0.3 mm. diameter, which could be electrically heated, fixed firmly at the top and weighted and dipping into mercury at the foot so as to make electrical contact and yet allow the wire to expand when heated. This is equivalent to a series of cells of the type shown in Fig 1 (b) arranged radially about the /

the hot wire. The wire was heated to 500°C and the tube allowed to operate for one hour, and during the next hour 20 mls. of gas were withdrawn slowly from the foot. It was found that within experimental error this gas was pure carbon dioxide. In this experiment, by careful adjustment of the heating current, it may be shown that a separation has occurred even without analysis; for then the wire initially uniformly red becomes bright red at the foot and, under favourable conditions, quite black at the top. This is because the hydrogen at the top, due to its higher thermal conductivity, cools the wire very efficiently while the carbon dioxide at the foot tends to retain the heat. The separation is really strikingly rapid; for example, if a mixture of bromine vapour and helium is used the difference in colour between top and foot is detectable after one minute and after ten minutes is virtually complete, the bromine condensing to liquid at the foot. The effect is, of course, much less for gases whose masses differ by less, and, as Clusius & Dickel were interested in the method as a possible means of separating isotopes, they now carried out a systematic investigation into the effect of varying the tube length and radius, the wire temperature, the total gas pressure, and so on, with the principal discovery that the longer the tube, the more complete was the separation. Technical difficulties prevented the construction /

construction of tubes of length greater than 9 metres, so they devised a means of connecting the foot of one tube with the top of the next by convection. Two channels connected the tubes, one being electrically heated and the other water cooled, and in this way the gas circulated between the two. After having tried many arrangements of tubes of different lengths they finally succeeded in getting 99.6% $H^{35}Cl$ from normal hydrogen chloride gas by using one 8 m. and two 6 m. tubes in series and 99.4% $H^{37}Cl$ by using one 9 m., two 6 m., and one 8 m. tube, also in series. Parallel arrangements were also tried with less success. It is to be noted that chlorine is a suitable gas for separation by a thermal diffusion method for the normal composition is approximately 75.7% of ^{35}Cl and 24.3% of ^{37}Cl so that neither is present at too low a concentration which would have made the thermal diffusion separation small.

The striking success of this, comparatively speaking, simple method attracted a great deal of interest and almost immediately Brewer & Bramley[31] described a modification of the method which consisted in substituting an internally heated central tube for the wire. This means that the distance between the walls of the gas-space can be reduced - which results in a greater separation - while by use of large diameter tubes the volume of gas used may even be increased. Onsager[32] has /

has shown, however, that theoretically the hot-wire method is more effective. A concentric tube system is on the other hand more robust and has been widely used.

One problem which has attracted much attention is the production in a state of purity of the carbon isotope ^{13}C. All gases are not equally suitable for use as "carriers" in thermal diffusion experiments (Harrison Brown[33]) and the gas chosen for carbon has usually been methane. W. Watson[34], A. O. Nier[35], and Taylor & Glocker[36] have worked on this separation but the results have not been very encouraging, the best results producing $^{13}CH_4$ at only four times its normal concentration of 1.1%, although the experiments have not been carried out on a scale comparable to that used by Clusius & Dickel. On the theoretical side the theory of the column has been formulated by Furry, Jones & Onsager[37]. Leaf & Wall[38], and Wall & Holley[39] have verified this theory to a certain extent by using it to calculate from their experimental results, in the diffusion of gases of similar molecular weight, the value of D_T (the thermal diffusion constant). This value is then compared with D_T calculated for rigid elastic spheres. Westhaver & Brewer[40] have gone into the question of power consumption as also did Clusius & Dickel[30] and Murin[78] and there is no doubt that it is a most uneconomical method, justified only by the results.

Brewer /

Brewer & Bramley[31] are of the opinion that the convection current does not run the whole length of the column but acts in a series of swirls, and have produced some evidence to support this based on the observation that the separation is increased by the inclusion of a limited number of baffles in the column. Another peculiarity of the column compared with the simple arrangement is that the separation is not independent of the pressure. For instance, in the methane experiments, there is a maximum separation obtained at 0.6 atmos.[35] Recent work on gases of similar molecular weight in which the separation depends rather more on the diameters and on the laws of interaction of the molecular species than on their weights have tiven some interesting results. Grew[42] found in mixtures of neon and ammonia that for 0% - 75% of neon the neon went to the top and for 75% - 100% of neon the ammonia went to the top. This is due to the change in sign of the thermal diffusion constant, a possibility which was indicated beforehand by Chapman and constitutes a good verification of his theory. Watson & Woernley[43] found that the thermal diffusion constant of ammonia containing 15% of $^{15}NH_3$ varied rapidly with temperature and changed sign at about room temperature. This effect was not anticipated but is attributed to the strong dipole-dipole interaction possible between $^{14}NH_3$ /

$^{14}NH_3$ and $^{15}NH_3$ molecules which is not taken into account in the simpler theory. Thermal diffusion results have in fact been widely used to study the laws of interaction of molecules, and, as similar information may be extracted from viscosity determinations, it has been usual to compare the results obtained by these two methods. In some cases agreement has not been very good and it has been suggested by Harrison Brown[44] that a possible source of this discrepancy lies in the fact that the mean temperature of the column may not be a representative temperature and suggests for this purpose a more complicated function of the temperatures of the hot and cold sides.

The separations obtained by this method, although much larger than those obtained by the simple method, are still apparently not complete enough to be of any industrial use. An attempt to push the separation still further has been made by Farber & Libby.[45] Whereas in a column, the convection is gravity controlled and so from that point of view is invariable, by placing the gas in a hollow disc which is rotated at high speeds much greater gravitational forces become possible. In the arrangement used one face of the disc was heated while the other was cooled, and, in accordance with expectation, it was found that the separation was increased, a maximum being observed at 10 × g; at higher speeds the separation fell off again. This arrangement /

arrangement from the point of view of the power used is even less efficient than the column although if a heat source were available at low cost it might well become a practical proposition. See also ref. 77.

In concluding this section it is to be noted that despite the larger effects obtained by thermal diffusion with convection it is commonly exceedingly difficult to obtain complete isotopic separations; but that in cases where there are two isotopes, both present at fairly large concentrations, separation is facilitated. Separations other than isotopic, however, can usually be obtained more economically by other methods and even in the case of isotopes it is not always the best method available.

(d) Thermal Diffusion in Liquids with convection.

The Clusius and Dickel method of multiplying the effect of thermal diffusion was found to be applicable to liquid systems very shortly after it had been found to work for gases. The way in which the increased separation arises is considered to be similar to the mechanism for gases, as described above. It turns out, however, that separations of reasonable magnitude are obtained only if there is a steep temperature gradient, and in practice this means that the distance between the hot and cold walls must be small.

The first experiments of this kind were carried out /

out by Clusius & Dickel[46] who placed the liquids in a long thin steel box whose internal dimensions were 1.5 m. x 20 mm. x 1 mm. One of the large outer faces could be heated and the other could be cooled. With such an arrangement it is not necessary, as is the case with a column with its heating element along its axis, to keep the tube vertical, and Clusius & Dickel investigated the effect of tilting it out of the vertical. They then discovered that the best results are usually not obtained in the vertical position but that each mixture has a characteristic angle at which maximum separation is effected. With this apparatus they caused in four hours a 3.6 fold increase in the concentration of 0.1 N NaCl at the foot of the tube, and obtained a smaller but quite definite effect in a 63% H_2O/D_2O mixture. They also investigated an acetone/water mixture which gave a large effect, the acetone, however, going to the top of the column, which they interpreted as being further evidence for the association of water in the liquid state.

The next investigation of the phenomenon was that of Korsching & Wirtz[47]. They carried out three distinct series of investigations. In their first experiments they employed a column quite similar to that used for gases, a hot wire being used or a copper pipe internally heated by oil. With this apparatus they caused definite separations of *n*-hexane/carbon tetrachloride /

tetrachloride and benzene/chlorobenzene mixtures. By varying the space between the hot and cold walls they were able to show that the closer the walls the greater the separation, as is to be expected. In the second series they used as hot and cold walls two long brass tubes of rectangular cross-section through which water could be circulated. These were separated by a thin rubber gasket which kept the tubes apart at their edges and left a space down the middle for the liquid. This apparatus was used to show that the process proceeds rapidly at first and then more slowly. Salt solutions were studied and it was demonstrated that sulphates, in general, sediment more rapidly than chlorides. It was also shown that in the diffusion of zinc sulphate solution more ^{64}Zn ions are found at the top of the tube and proportionately more ^{66}Zn and ^{68}Zn ions at the foot. A few substances of high molecular weight were also studied and shown to diffuse quite normally. This work has been extended by H. E. Carr[48], who used a similar apparatus. He demonstrated that for zinc sulphate solution (0.6M) the optimum separation is obtained with a tube slope of about 50° and that the separation/concentration curve shows a maximum at 0.6 M.

In their latest experiments Korsching & Wirtz have used a new type of column made from two concentric metal cylinders fitting closely the one inside the other in such a way that a gap of about 0.25 mm. is left /

left between them. Using a series of such columns they have successfully demonstrated the ability of thermal diffusion to separate some mixtures which are otherwise difficult to separate. For example, from the constant boiling point mixture of 95.6% alcohol in water there was obtained 99.8% alcohol in one experiment, and in another a small amount of thiophene was almost completely removed from benzene. They also attempted to separate two substances dissolved in the same solution using cholestatrienon and cholestenon dibromide in benzene, using the fact that they sediment at different rates, an experiment which was partially successful.

Now, whereas a metal column is more efficient than a glass one from the thermal conductivity point of view, a glass column also has its uses for it enables one to observe many interesting changes which take place in solutions. A glass column, for instance, was successfully used by Taylor & Ritchie[49] to demonstrate the thermal diffusion of a mixture of hydrochloric acid and cobalt chloride in water. A solution of cobalt chloride in water or dilute hydrochloric acid is pink (Co^{++}) but in concentrated hydrochloric acid it is deep blue due to the formation of complex cobalt ions. A solution of intermediate tint was introduced into the tube and using a gradient of 85°C. a definite separa- was detected after two hours, the solution at the top becoming /

becoming pink while that at the foot became blue. Similar experiments were carried out with cupric bromide and hydrobromic acid which is brown in presence of much hydrobromic acid and blue in smaller hydrobromic acid concentrations. They also concentrated copper sulphate to the point at which it crystallised out at the foot of the column. Gillespie and Breck [50] using a similar apparatus were able to observe the partial hydrolysis of ferrous and ferric chlorides, although this was not sufficient to invalidate their results. They investigated aqueous solutions containing a salt and an acid and found that such solutions showed a wide divergence of behaviour. For example, ferrous chloride in water concentrated at the foot, if present alone; but in presence of 1 N H_2SO_4 it did not concentrate at all while in presence of 1 N HCl it concentrated at the top. In the case of zinc chloride, on the other hand, the enrichment which takes place at the foot in presence of a trace of acid (to prevent hydrolysis) is considerably greater in the presence of 1 N HCl. Finally, in the case of acetic acid and sodium acetate, the results tend to show that the two solutes diffuse independently.

A completely new field was opened up when Ballay [51] in 1926 demonstrated the existence of the Soret effect in molten metal alloys. The effect was small but quite definite and more or less as a consequence of this /

this work the Soret Effect has been invoked as the cause of the segregation which is observed in steel ingots. The supporters[52] of the theory regard the gradient as being established between the cool outside of the ingot and its molten interior. However, the concentration of the segregating substances (Si, P, etc.) is usually exceedingly small, a fact which tends to diminish the magnitude of the effect. A committee of the Iron & Steel Institute was set up to study the problem under Dr C. H. Desch who, after a critical survey of all available data, came to the conclusion that the Soret Effect was not concerned in the segregation[53]. However, no data existed for the convective thermal diffusion of alloys, so some experiments were carried out for the committee by M. Ritchie using 1.5% Zn in mercury (which is a comparable system liquid at a convenient temperature). The results were uniformly negative, but it is possible that the high thermal conductivity of the amalgam rendered the gradient ineffective although, of course, the same thing may be said of the ingots. Similar phenomena occur in meteorites and in rock magmas[54] for which also, if they are not to be explained by the Soret effect, another explanation will have to be found.

It is to be noted that in all these experiments attention has been mainly directed towards the separation observed at equilibrium. From this point of view it /

it is evident that the behaviour of aqueous solutions containing one solute is rather erratic while that of those containing two solutes is as yet unpredictable.

An attempt at the theory of the process has been made by Debye[55], Hiby and Wirtz,[56] and Waldmann[57]. These are all essentially mathematical and will not be discussed in this historical section.

2. CHOICE OF SOLUTE, SOLVENT, ETC.

Reviewing the work on gases described above, it is seen that the results may profitably be considered in two related sections. First, the method has made the practical separation of some binary gaseous mixtures so efficient that isotopic and other separations may be accomplished with an ease and rapidity certainly not visualised a few decades ago. Secondly, the equilibrium separations attainable in certain systems considered theoretically yield a variety of information regarding the interactions and field forces of the colliding gas molecules. As has already been mentioned, the theory of the process in gases is well advanced but the comparison of gas systems with liquid systems has not in the past been attended by much success as is shown, for example, by the old controversy regarding the analogy between gas pressure and osmotic pressure. The underlying reason for this emerges from some recent work which has shown that a substance in the form of a liquid just above its melting point resembles in many respects the solid, although at higher temperatures there is increasing approach to the gaseous condition; thus only at higher temperatures near the boiling point does the heat motion approach the free translation /

translation and free rotation of gaseous molecules, as is made evident, for example, by the fact that the specific heats of liquids at high temperatures approaches that of the corresponding gases (See, for example, Frenkel[58]). As far as a solute is concerned J. Kendall[59] has shown that all the evidence points to the dissolved substance as being in the liquid condition. Nevertheless, in spite of these differences between liquid and gas some general principles common to both may be expected to apply. Thus in liquids, as in gases, the rate of concentration of a constituent must a priori be considered to depend on the sizes, masses and field forces of the interacting molecules; where two dissolved substances are present the rates of concentration will depend on the nature of the solute and solvent molecules and it is therefore to be expected that certain conditions might arise whereby the separation of certain constituents might be facilitated. Such separation would then be if no little importance in various practical operations, more particularly those in which fractional crystallisation is difficult as in the case of various sugars and sugar mixtures. Such a system containing three molecular species arises more commonly in liquids than in gases, but in the few cases which have been investigated such as the isotopes of Krypton[60] the molecules have all been found to concentrate /

concentrate at different rates. Returning to liquids, diffusion, and with it thermal diffusion, is one of the "dynamic" properties of a liquid. Bauer, Magat and Surdin [61] have shown that certain liquid properties such as molecular volume, compressibility and surface tension may be expressed with fairly good approximation by one single law for all liquids. These, however, are "static" properties: the "dynamic" properties which include (as well as diffusion) viscosity and heat conduction cannot be expressed by any such general relationship. There are exceptions to the "static" property rules usually where definite and pronounced intermolecular reactions exist, and these divergences must persist in the less regular "dynamic" properties also, which accordingly may be expected to be, in such cases, of an even more complicated nature. Osmosis is a phenomenon which is really very closely allied to diffusion; in fact, as was pointed out by J. J. van Laar [62] , it is a direct consequence of it and cannot exist in an isolated solution. Some connection may then be logically expected between Thermal Diffusion and Osmosis although certainly not of the simple nature indicated by van t'Hoff.

This work was commenced in the first instance with a view to the possible application of the method to the separation of mixtures of sugars. Such mixtures are difficult to separate; for example, fractional crystallisation /

crystallisation usually fails, due to the formation of syrups, and, on the other hand, few free sugars distil without decomposition even under high vacuum. Whereas this determined the choice of solute and solvent in the first instance further consideration seemed to indicate that such a system was in fact a most suitable one on which to commence the study of the phenomenon. In the first place it seemed wise, in the early stages at least, to confine the study to non-electrolytes: this, it was hoped, would simplify not only the experimental results obtained, but also their theoretical interpretation. Secondly, the involatility of the sugars seemed to offer some advantages, there being no possibility of the solute distilling off, condensing and running back into the solution. Thirdly, the sugars are remarkably soluble and a very wide range of concentrations may be studied and they constitute a series of compounds of much the same type with a wide range of molecular weights. The upper members of the series, which have large molecular weights in comparison with water, may be expected to give large effects. In particular, the well known fact that the sugars in dilute solutions give normal values for the osmotic pressure seemed to be propitious; for, as has been mentioned before, diffusion is intimately concerned with osmosis and accordingly in such solutions it might be expected to proceed in a comparatively simple manner.

Further, /

Further, on the theoretical side, it seemed reasonable to suppose that such constants as viscosity and diffusion coefficients might be required for the solutions studied and over a wide range of concentration and temperature. These results as it happens are available for the sugars; as a matter of fact the data for other substances is much less complete. In addition, sugar solutions may be readily analysed by means of the polarimeter or refractometer or by a variety of other chemical methods.

Just why dilute solutions of sugars in water constitute an apparently ideal system is not at once clear. Water has in the past been regarded as perhaps the most complex of the common solvents in that its properties and those of its solutions appeared to diverge most from the regularities of the ideal solvents. Such irregularities were then loosely related to "solvation" and "association". In recent years, however, study of such divergence from the ideal has so progressed that the main features of solvation and association are becoming clear. In 1937 Bernal[63] outlined a geometrical theory of the liquid state, dealing with the average distribution of molecules round a given molecule as governed by a co-ordination number giving the number of surrounding immediate neighbours and an irregularity function fundamentally characteristic of the liquid state. The liquid may thus be regarded as pseudo- or quasi- /

quasi-crystalline. If definite directed forces exist such as homopolar bonds, polarised ionic bonds, or the weaker hydrogen or hydroxyl bonds, then the co-ordination number will tend to be reduced and this will show in thermal and allied properties, e.g., viscosity and diffusion. In the particular case of water Bernal & Fowler (1933)[64] have shown that certain results may be best explained by a fourfold co-ordination at low temperatures due to the formation of hydroxyl bonds. Briefly, then, water is characterised by a large number of bonds through hydrogen. This must also be true of the sugars in the dissolved ("liquid") condition, and since it has become clear that in order to mix ideally substances must be similar in character, the actual type of character being of secondary importance only, the reason for ideal behaviour at low concentrations is readily understood. It was hoped thus to eliminate any complications due to association or disaggregation.

Finally, in view of the convenience of using high pressure steam and tap water to establish the gradient it was decided to proceed with aqueous sugar solutions.

A start was then made with the measurement of the initial rate of separation, extrapolated to zero time if possible, when the concentration is definitely known. In the equilibrium state there is a concentration gradient along the length of the tube, and, as a result, the viscosity, density, etc., vary with position. /

position. Clearly it would be very difficult to treat such a system theoretically.

EXPERIMENTAL

(a) The Thermal Diffusion Column

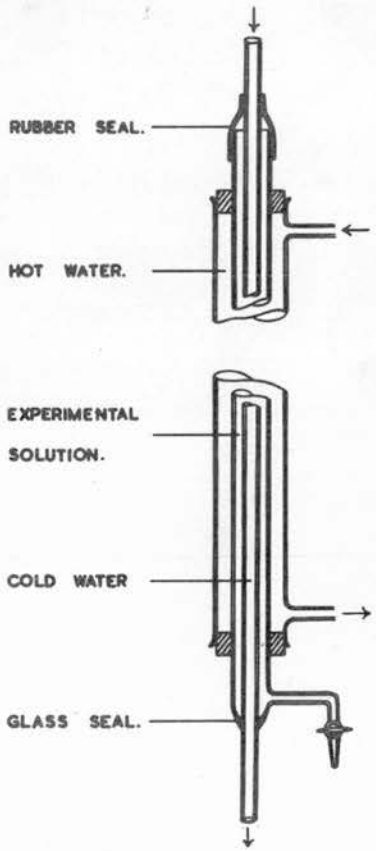


FIG. 2

The thermal diffusion column used (see Fig. 2) was made of glass because it was desired to carry out all the experimental work which might be necessary with the same apparatus and to have made it of metal would necessarily have confined the study to solutions non-corrosive towards metal. The great advantage of metal over glass is that it has a much higher thermal conductivity and for a given wall thickness a higher proportion of the imposed gradient actually operates on the solution. This can be partly offset by the use of very thin-walled glass and this, in fact, was what was done, although this /

this made construction more difficult and the column more fragile.

CONSTRUCTION. A length (5 ft.) of glass tubing of about 1 cm. external diameter was taken and a small bulb blown in it about 6" from one end. Another length of slightly greater diameter tubing, such that the radial gap was about 0.5 mm., was now slid over this tube until its open end came in contact with the bulb, when the two were sealed together there. A side tube was attached to the outer tube as close to the junction as possible, to give access to the annular space. Afterwards a small tap was attached to this tube and bent downwards. At the other end, the inner tube projected beyond the outer, but, in order to allow for expansion and contraction, the two were not sealed together in this case. A piece of rubber tubing of suitable diameter was used to close the annular space. This piece of rubber tubing, which was of heavy gauge, was permanently attached to the tube. It was necessary to break the air seal to permit of the introduction and removal of solutions but this was done by inserting a thin wooden splint between the glass and the rubber. Before commencing a determination this splint was removed and the rubber tube then automatically set the central tube back to the same position, thus ensuring that the gap conditions were always the same throughout the various series of experiments. It also served to prevent /

prevent evaporation and to prevent water condensing higher up on the cold central tube and running into, and thus diluting, the solution. A copper jacket was now placed round the tube, holding it by rubber stoppers; it was so arranged that as little solution as possible, at the foot of the column, remained unheated.

FILLING. In order to fill the column a long rubber tube was attached to the tap. This led through a glass tube into a flask containing the solution which was raised to a level higher than the top of the column. In this way the solution was siphoned into the column through the tap at the foot. It was not found possible to introduce the solution through the rubber seal at the top as the annular space was too narrow and air locks formed.

HEATING, ETC. In all experiments the water which was circulated through the outer jacket was warmer than that which passed down the central tube. Sometimes steam was used and in conformity with this scheme it was always passed through the outer jacket. It will be noted that in both cases the water enters at the top and leaves from the foot. This was a matter of convenience only, for the apparatus was mounted above a sink in order that the waste water might be easily removed. However, to make sure that the outer jacket was full of water, a long glass tube was mounted beside the column and connected to it to indicate the level of the /

the water inside. The column was kept full by constricting the water exit by means of a rubber tube and screw clip.

Thermometers were placed at the entry and exit of both cold and hot water (or steam). It was noted that there was quite a large difference in temperature between the top and the foot in both cases. This was considered most undesirable for it meant that the gradient was much less at the foot of the column than at the top. The obvious remedy was to increase the speed of the water. This caused the rubber tubing, used up to this time, to burst, so it was all removed and replaced by 0.9 cm. (external) diameter glass tubing sections connected together by canvas-reinforced rubber hosepipe which was wired on with 1/16" copper wire. The water could now be passed very rapidly and even if steam were passed down the outer tube, cold tap water rose only about $1^{\circ}C.$ in passing down the column. Later on streams of hot water at various temperatures from 10° to $100^{\circ}C.$ were required. To obtain these, a series of gas-heated copper coils and long gas-heated copper tubes were used, and, in order to allow the water to heat up, its speed had once more to be reduced, and the above-mentioned undesirable feature arose once more. In the later experiments it was found that matters could be improved in the following way. The tube was first wound with asbestos string. (This /

(This itself helped to reduce heat losses.) On top, there were wound"Nichrome-on-Asbestos String" electric heating spirals (1 kw.) Four such spirals were fitted to the column along its length. By judicious use of these it was found possible in many cases to so heat up the outer water stream in its passage down the column that the temperature difference at the top was the same as at the foot. In this way the gradient remained constant along the length of the tube. In these investigations of the effect of mean temperature and of gradient the question arises - Does the mean of the temperatures of the cold and hot water streams bear any relationship to the actual mean temperature of the contents of the column? In an attempt to answer this question the following experiment was carried out. A long glass tube was attached to the outlet tap and led up to the top of the column. The column and this tube were now both filled with distilled water and brought to the same temperature. A cold water jacket was fitted to this external tube for the purpose. On comparing the levels in the tube and the column it was found that the level in the column was 1.80 cm. higher than that in the glass tube due to the effect of capillarity. Various gradients were then applied to the column by means of cold water and hot water (or steam) and due to the decrease in density of the water in the column, this difference in levels increased as the mean temperature /

temperature of the column was increased. Applying the relationship $g\rho_1 h_1 = g\rho_2 h_2$ the density of the water in the column could then be calculated, and reference to International Critical Tables gave the corresponding temperature.

Results

Temperature of external tube (constant) 7°C.

Length of heated liquid in diffusion column 128.0 cm.

Diffusion /

Diffusion Column							Diffusion Column plus external tube			
Inner Tube Temperatures °C.			Outer Tube Temperatures °C.			Mean	Difference in Levels	Difference due to density only	Calculated density in column	Corresponding mean temperature
Top	Foot	Mean	Top	Foot	Mean	Temp.				
7.0	7.0	7.0	7.0	7.0	7.0	7.0	1.80	0.00	0.99993	7.0°C.
"	7.0	7.0	23.0	23.0	23.0	15.0	1.95	0.15	0.99865	17.8°C.
"	7.0	7.0	29.0	29.0	29.0	18.0	2.05	0.25	0.99798	21.2°C.
"	7.5	7.3	44.0	44.0	44.0	25.7	2.15	0.35	0.99720	24.5°C.
"	7.5	7.3	51.0	51.0	51.0	29.2	2.25	0.45	0.99643	27.4°C.
"	8.0	7.5	60.0	60.0	60.0	33.8	2.45	0.65	0.99488	32.5°C.
"	8.5	7.8	88.0	83.0	85.5	46.7	3.20	1.40	0.98913	40.8°C.
"	9.0	8.0	100.0	100.0	100.0	54.0	4.00	2.20	0.98307	60.0°C.

Table I

Comparing the mean temperatures obtained by the two methods, it will be noted that:-

1. At low gradients the mean temperature calculated from the density is higher than that observed. This was expected for although the tubes of the column were both of very thin glass, the outer one was certainly the thinner.

2. At higher temperatures the calculated mean temperature is lower than that observed. For example, in the second last row of the table, despite the electric heaters round the column, the temperature fell by 5°C. This was partly due to the fact that the cold water exerted a relatively greater cooling effect than, say, in row 2, because in the former case the gradient is greater; but it was also partly due to the decrease in the rate of flow of the hot water. This was because the water entering at 88°C. could not be made to flow any faster, for the gas heating system could not then keep the temperature up. Addition of further heaters caused no improvement, for this merely resulted in a lowering of gas pressure in all the others already in use.

3. In the last case, where steam is used, it is seen that the calculated temperature is once more greater than that observed. This was due in the first place to the relative thinness of the outer tube already mentioned, in the second to the rate of passage of steam which /

which could be very rapid since it was supplied at high pressure from the departmental boilers, and in the third to the fact that the steam was really a much more efficient method of heating than water in that it could liberate its latent heat of vaporisation when it condensed on the cooler diffusion column.

DIMENSIONS. The diameter of the inner tube was determined by means of a micrometer screw gauge, being the mean of 50 determinations along the length of the tube. In order to find the average annular distance between the tubes, the weight of water filling that length of the space which was heated was obtained. From these figures the average radial gap can be calculated.

Column I Temperature 12°C.

External diameter of inner tube	9.806 mm.
Weight of water filling heated length (W)	26.863 g.
Length of heated space	1250 mm.

Now if r_e = external radius of inner tube

r_i = internal radius of outer tube

V = volume of annular space heated

h = length of annular space heated

$$V = \pi (r_e^2 - r_i^2) h$$

$$\therefore r_e = \left(\frac{V}{h\pi} + r_i^2 \right)^{\frac{1}{2}} = \left(\frac{26.86 \times 10}{1250 \times 3.142} + 4.903^2 \right)^{\frac{1}{2}} \text{mm.}$$

i.e. $r_e = 5.556$ mm.

$\therefore$ Radial gap $= (5.556 - 4.903) = 0.653$ mm.

In this determination the figure W was suspect. The method used for the determination of W was as follows. The tube was filled with distilled water until just level with the top of the outer jacket. The water was then run out into a weighed beaker until the level had fallen to the foot of the outer jacket, about five minutes being allowed for drainage, and weighed. It seemed probable, however, that even with this time for drainage some water might be retained by the column by surface tension at the places where the tubes are closest. An alternative method of determining the volume, which gets over this difficulty, was then tried. Unfortunately it could not be used for column I, because column I was broken before the method was devised.

Column II was thoroughly washed with hot distilled water and dried by drawing air through it overnight. A 30 ml. burette was attached by a long rubber tube to the tap at the foot of the column. Distilled water was placed in the burette and run out until it had filled the rubber tube, side tube and the small space of the main tube as far as the foot of the outer jacket. The level in the burette was then noted. Water was run into the column out of the burette until the level reached the top of the jacket when the burette was read again. The difference in the burette readings gave the volume of the annular space heated. This volume was also determined by the weighing method used for tube /

tube I. The result (27.560 g.) was as anticipated lower than that obtained by the burette method and was not used in the calculation.

Column II.

External diameter of inner tube	9.806	mm.
Volume of water filling heated length (V)	28.20	ml.
Length of heated space	1264	mm.

$$r_e = \left(\frac{V}{l\pi} + r_i^2\right)^{\frac{1}{2}} = 5.582$$

$$\therefore \text{Radial gap } (r_e - r_i) = 0.679 \text{ mm.}$$

It will be noted that Column II was very similar to Column I in dimensions. This was reflected in the experimental results.

(b) Methods of Analysis.

The object of all the analyses was to determine the concentration of the solute at the foot of the column. It had been found by the burette method described above that the volume of the side tube between the column and the tap was 0.46 ml. or approximately 8 drops. In order to get a sample representative of the lowest region, two procedures were used, depending on the circumstances.

(1) If a series of samples were being taken separated /

separated by short time intervals (e.g. at 0, 2, 4, 6 minutes), samples of eight drops were run out. It was then found that the sample taken at 2 minutes had the same composition as the original solution. This indicated that the solution in the side tube had not changed in composition in the two minutes during which it had been in the side tube. The next sample, which was actually withdrawn at 4 minutes, but had entered the side tube at 2 minutes, had, presumably, not changed in composition either and was representative of the concentration within the tube at time 2 minutes. This argument, which implies that the solution moves bodily, is considered to be justifiable on account of the narrowness of the annular space and of the side tube.

(2) On the other hand, if samples were being taken at intervals of anything greater than 15 minutes this procedure was found unsatisfactory. For then the solution in the main tube slowly diffused into the side tube, which then contained a solution of varying composition. In such cases all the solution in the side tube (8 drops) was discarded and a further 8 drops of solution were used to wash it out, and then an 8 drop sample was taken. This sample, then, was representative of the concentration in the column at the time at which it was withdrawn.

It is desired to emphasise at this stage that the quantity /

quantity of solution available for analysis was in all cases small. When analysis was performed by means of the Pulfrich refractometer the solution could be analysed just as withdrawn, but in all other cases it had first of all to be diluted. For this purpose 0.5 ml. was measured as accurately as possible with a graduated pipette and made up to an appropriate volume in a graduated flask. However, not all the solutions used were really suitable for pipette measurement. Some were quite syrupy; some came out of the column quite warm due to the type of gradient being used. There were thus unavoidable errors due to evaporation, retention of abnormally large quantities of liquid by the pipette and so on. In general it is considered that the greatest relative error in the analysis arises in the sampling, although every precaution such as keeping the pipette free from grease, etc., was observed.

ANALYSIS BY PULFRICH REFRACTOMETER.

Solutions containing only one solute may be analysed by means of their refractive index. This method was used for solutions of sucrose, glucose, xylose, raffinose and glycerol. The Pulfrich refractometer was most convenient for the purpose, for a sample of eight drops, such as was available in these experiments, was sufficient for the determination. The refractometer, however, required to operate at a steady temperature, and /

and for this purpose a stream of water was passed through its water jacket from a thermostat. The thermostat was a large copper tank, heated by gas, the flow of which was controlled by means of an expanding contrd in which chloroform (containing 1% alcohol to prevent oxidation) was the expanding substance. The chloroform was sealed in by mercury which in its turn interrupted the gas supply. The thermostat was set to 25°C and the temperature in the refractometer water jacket was then 24.75°C. and this was taken as the standard temperature for all subsequent work.

Preliminary experiments showed that one minute is sufficient for the small 8-drop sample to reach the temperature of the instrument, and when samples were being taken at 0, 2, 4, 6, 8, etc. minutes, to avoid evaporation errors, it was the practice to analyse them as the run proceeded. The cell of the instrument was cleaned out after each reading by sucking the solution out of it by a tube connected to a water pump, washing three times with distilled water which was rapidly removed in the same way and drying with several small swabs of cotton wool. The light source used was an electric sodium vapour lamp.

The actual procedure in all cases was to prepare a series of samples of known composition and determine their refractometer reading. In the first series of solutions examined (sucrose), the refractive indices corresponding /

corresponding to these readings were obtained from the tables provided, but as it was found that the plot of refractuve index against concentration was the same type of curve as the plot of the refractometer reading against concentration, the refractive indices were not worked out for any other solutions. From this graph the concentration corresponding to any observed refractometer reading may be read off directly. The concentration units in all cases are gram molecules per litre. The concentration of the water is also required in the same units and this necessitates the determination of the specific gravity of the solutions used. A 25 g. specific gravity bottle was used for this purpose. All specific gravity determinations were made at 15°C. and are relative to water at the same temperature.

Each solution, if it was to be examined with respect to the initial rate of the process, was then placed in the column, the steam and cold water turned on, and samples withdrawn at short intervals. The samples were analysed and the concentrations obtained plotted against the time, and from this graph the initial rate was obtained.

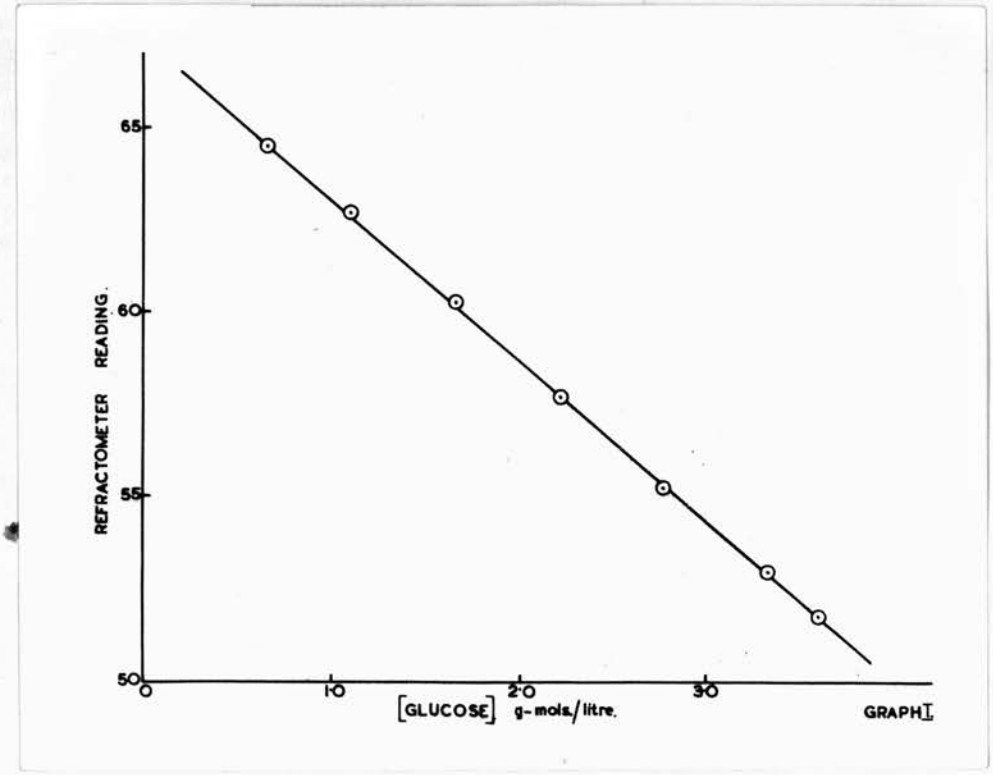
The results of a typical experiment are now given in order to show the methods of calculation, etc.

Solutions /

Solutions of Glucose (Mol. Wt. 180.2) in water.

[Glucose] g./litre	Specific Gravity	[Water] g./litre	[Water] g.mol./ litre	[Glucose] g.mol./ litre	Refracto-meter Reading (24.75°C.)
120	1.047	927	51.4	0.666	64°29'
200	1.076	876	48.6	1.110	62°40'
300	1.109	809	44.9	1.665	60°15'
400	1.148	748	41.5	2.220	57°41'
500	1.185	685	38.0	2.775	55°15'
600	1.220	620	34.4	3.330	52°57'
650	1.237	587	32.6	3.605	51°45'

The [Glucose] is then plotted against the refractometer reading in graph I.



Remarks:-

Column I: Pure glucose was weighed out, dissolved in hot distilled water, cooled, and made up to the required volume in a standard flask.

Column V: g.mols./litre = 10 x g./100 mls. ÷ 180.2 (Mol. Wt. of Glucose)

Column II: By 25 ml. specific gravity bottle. Example: 50 g./100 ml. soln.

Wt. of bottle	13.435g.	
" " " + water @ 15°C.	38.453g.	∴ wt. of water filling bottle 25.018 g.
" " " + 50g./100 ml. soln.	43.105g.	∴ wt. of soln. filling bottle 29.670 g.

Hence specific gravity = 29.670 ÷ 25.018 = 1.185 at 15°C.

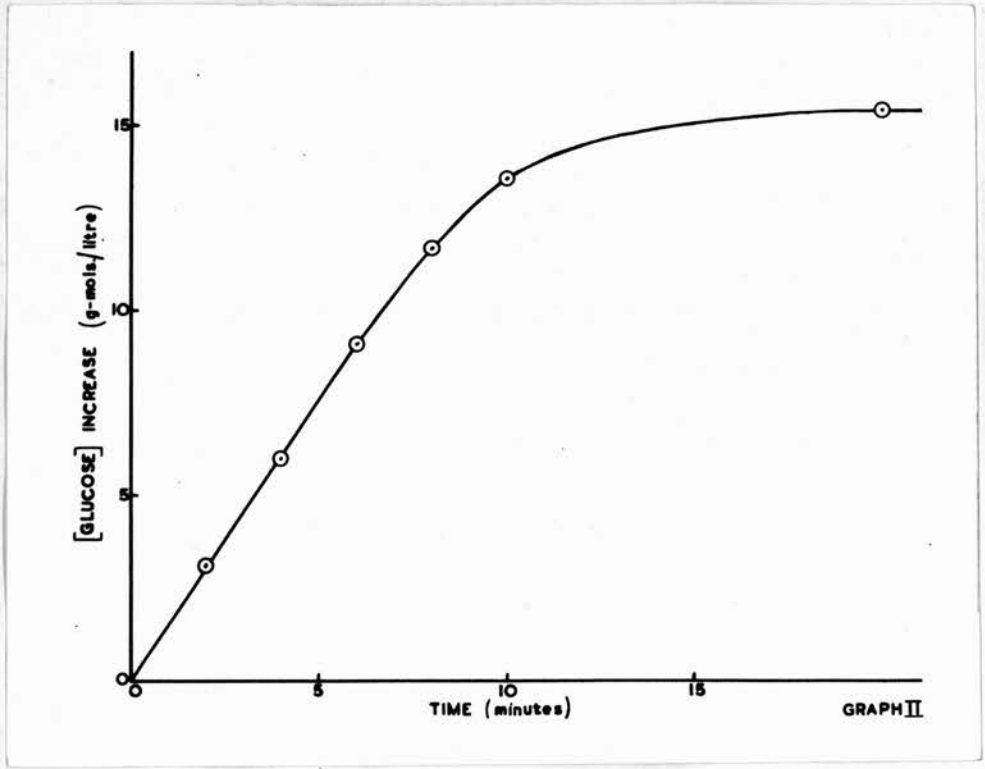
Passing on to a typical experiment with the column, the following results were obtained with 40 g./100 ml. solution of glucose.

Time (mins.)	Refractometer reading	[Glucose] g-mol./litre from Graph I.	Increase in [Glucose]
0	57°41'	2.220	nil
2	57°33'	2.251	0.031
4	57°25'	2.280	0.060
6	57°17'	2.311	0.091
8	57°10'	2.337	0.117
10	57°05'	2.356	0.136
20	57°00'	2.374	0.154

Remarks /

Remarks.

In practice a portion of graph I was considerably enlarged in order to read off these values for column III The figures in column IV are now plotted in graph II.



GRAPH II

It will be seen that the rate falls off with time as expected. In this case the rate is however almost constant over the first 6 minutes, and this was quite usual. In cases where the curvature extended as far as to zero time, an attempt was made to draw the tangent to the curve at the origin. The rate was expressed /

expressed in g.mol./litre per minute.

In the above example -

Rate = 0.015 g.mol.glucose/litre/minute.

Analysis of Solutions of Acetone.

In the case of acetone and water mixtures it was not possible to use the refractometer because the cell was fixed to the prism by "Durofix" which is soluble in acetone. Accordingly a chemical method was used, based on that given by Munro[65], which involves the quantitative oxidation of the acetone by alkaline hypoiodite, acidification, and titration of the unused iodine by sodium thiosulphate.

Procedure

(a) A small sample was withdrawn from the tube. This varied from 10 to 20 drops depending on the solution. Solutions containing much acetone gave very small drops and 20 were required to furnish 0.5 ml; in any case, an attempt was made to keep the volume withdrawn constant at about 0.6 ml. Of the sample, 0.5 ml. was appropriately diluted in a standard flask immediately (to avoid evaporation), and a definite volume of this solution was then used for the estimation, such that the amount of acetone present was between 10-15 mg.

(b) Into a 250 ml. conical flask was measured accurately 25 ml. of N/10 iodine and approximately 10 ml. of 40% sodium hydroxide (approx. 10 N) which were mixed, and /

and then at once the sample for analysis was measured into the mixture. It is important that the hypoiodite should not stand in air for any length of time for it is converted into iodate and iodide which have no effect on acetone, although they are reconverted to iodine quite smoothly on acidification. Iodoform precipitates out immediately, but the mixture was left for 30 minutes in the cold, as part of the standardised procedure.

(c) 10 x 1 ml. portions of conc. HCl (approx. 10 N) were then added from a burette at minute intervals, the solution being cooled between additions by running water This procedure ensures that the heat liberated during the neutralisation of the alkali by the concentrated acid is not sufficient to volatilise iodine. When the solution was almost nautral it turned from yellow to brown and addition of HCl was stopped and the solution thoroughly cooled. (Depending on the actual quantity of NaOH added, more or less than 10 mls. of conc. HCl were required). After cooling (for about 5 minutes), 1.5 mls. of conc. HCl was added further in excess. (This was done because it was noted that the earlier determinations were somewhat erratic and this was traced to the fact that not all the iodine present had been liberated, the solution on testing with litmus paper being found to be still alkaline - although brown coloured). The solution was then titrated immediately with /

with N/10 sodium thiosulphate using starch at the end point. A control determination was also carried out by omitting the acetone, and by difference the amount of iodine, used by the acetone was obtained in terms of mls. of thiosulphate. In order to calibrate these titration figures, a series of samples of known composition were prepared and put through the same procedure. In practice the determinations were run in pairs - an unknown sample with a known sample of approximately the same composition - to eliminate any possible variation in the conditions. All titration figures were now converted by proportion to the values which they would have had if 0.01 ml. of the original solution (before dilution) had been used. This gave numbers of a suitable magnitude. These corrected titration figures, in the case of the samples of known composition, were now plotted against the concentration (g.mols./litre) of acetone in the mixture - (Graph III). This graph was then used to convert the titration figures of both the "known" and the "unknown" samples into g-mols./litre of acetone

In the case of acetone solutions, the initial rate was taken as the change produced in 10 minutes, so that two determinations only were carried out on each solution, viz., time zero and 10 minutes.

Results.

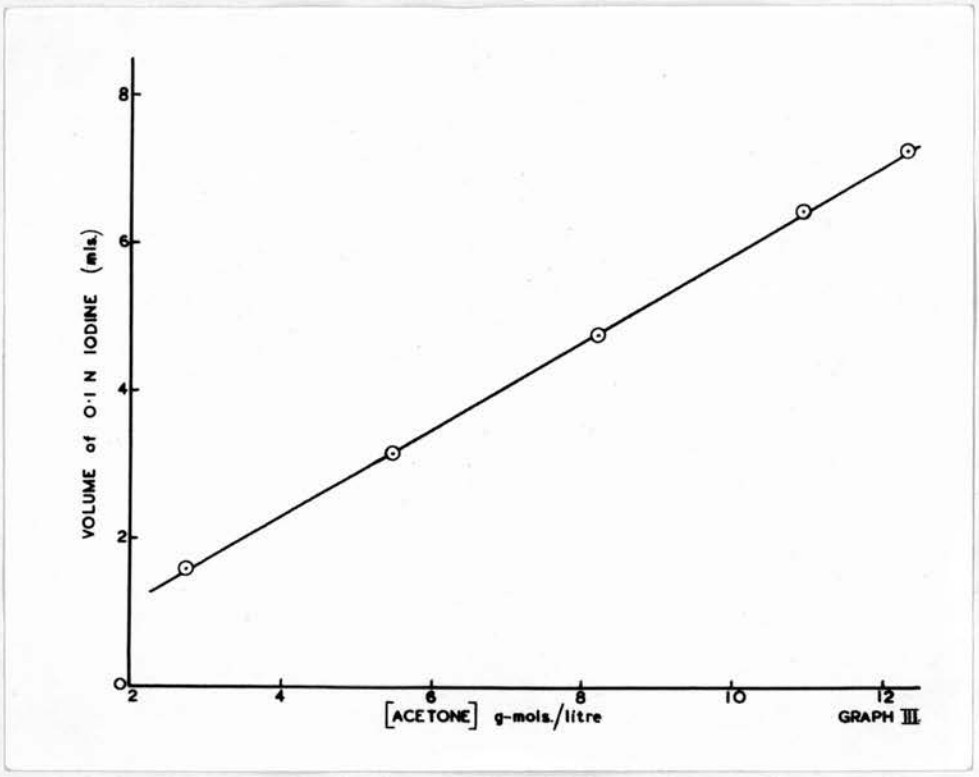
It is to be noted that the acetone concentration at the /

the foot of the column decreases during each experiment. Acetone solutions were made up by taking a known volume of acetone and making up to the required volume in a graduated flask with water. In order to obtain the g.mols./litre concentration of water and acetone, it is necessary to know the density of the acetone in addition to the density of all the solutions used. The figure used was 0.7967 which was determined directly by specific gravity bottle.

Calibration figures.

[Acetone] mls. in 100 ml. solution	Specific Gravity	[Acetone] g.mols/ litre	[Water] g.mols/ litre	mls. of N/10 I_2 used by 0.01ml. of solution
20	0.9810	2.741	4.559	1.591
40	0.9582	5.481	3.548	3.148
60	0.9274	8.228	2.493	4.760
80	0.8775	10.96	1.332	6.933
90	0.8417	12.34	0.692	7.248
(100)	(0.7967)			

These results are now graphed.



GRAPH III.

Typical Analysis. Solution 40 mls. acetone/100 mls. solution.

(a) Solution before diffusion) 0.5 ml. made up to 50 mls.
(b) " after ") with distilled water.

4 mls of diluted (a) + reagents used of $\frac{N}{10}$ $Na_2S_2O_3$ ... 10.37 ml
4 mls " " (b) + " " " " 11.43 ml
4 mls distilled water + " " " " 22.96 ml
∴ diluted (a) used of $\frac{N}{10}$ iodine 12.59 ml
∴ " (b) " " " " 11.53 ml

$\therefore$ 0.01 mls. of original (a) would have used

$$12.59 \times \tfrac{1}{4} \times \frac{0.5}{50} = 3.148 \text{ mls. } \frac{N}{10} I_2$$

$\therefore$ 0.01 mls. of original (b) would have used

$$11.53 \times \tfrac{1}{4} \times \frac{0.5}{50} = 2.882 \text{ mls. } \frac{N}{10} I_2$$

Referring now to Graph III

Acetone concentration in (a) = 5.45 g.mols./litre
Acetone " " (b) = 5.00 " "

$\therefore$ Initial rate of concentration = 0.45 g.mols/litre/min.

Analysis of Solutions containing Glucose and Sucrose.

A method using the polarimeter was employed. The solution was diluted and its polarimeter reading taken ("Direct" reading). It was then "inverted" with acid and cooled and its new reading taken ("Invert" reading) The change in rotation Direct — Invert is proportional to the sucrose present. Having thus determined the amount of sucrose, its contribution to the rotation of the original solution could be calculated. The rotation due to the glucose could then be obtained by difference /

difference, and the amount of glucose present calculated.

Method. A sample of about 10 drops was withdrawn from the column and placed in a weighing bottle. 0.5 ml. of this solution was removed by a blow-out pipette and placed in a 7 ml. graduated flask (which was specially made for the purpose - the polarimeter tube used having a capacity of 7 mls.). After dilution to the mark and mixing, this solution was placed in the 10 cm. polarimeter tube which had a water jacket. By means of a circulating pump, water from a gas-heated thermostat, similar to that described above for the Pulfrich Refractometer, was caused to flow through the jacket and by this means the solution was brought to 25°C. (thermometer in the actual solution) when a reading was taken ("Direct").

The polarimeter used was a Hilger Instrument, and could be read to 0.01° by means of a vernier. The light source was a quartz mercury vapour lamp which ran at about 2 amps on 100 volts D.C. A filter was used which selected the mercury green line 5460°A: the instrument is provided with suitable prisms for use with green light.

As much of the solution as possible was now poured out of the polarimeter tube into a clean vessel and of it 6.5 ml. was taken with a graduated pipette and transferred to a clean 7 ml. "inversion tube."

The /

The inversion tubes were specimen tubes about 3 inches long and ½-inch in diameter, which hold about 8-9 mls. They were calibrated and marked to contain 7 mls. of liquid. The open ends of the tubes were flanged and a rack was made out of sheet copper to hold ten of them, so that they were immersed up to the graduated marks in a water bath at 70°C. This bath was a white enamelled "can" of cylindrical shape, 8" high and of 8" diameter, which was heated from below by 2 x 500 watt electric spirals and was thermostatically controlled, by means of an expanding control in which the expanding substance was mercury. This operated a Sun-Vic hot wire vacuum switch which controlled the electric heaters. No stirring was necessary as convection is considerable at 70°C.

To the 6.5 mls. of solution in the inversion tube was added 0.5 ml. of concentrated HCl and the tube placed in the rack in the bath for 30 minutes. After this time the tube was withdrawn, cooled and the contents made up to the 7 ml. mark to correct for evaporation losses. The polarimeter reading of this solution was then taken ("invert" reading).

The zero of the polarimeter being -0.36, this number was added to each polarimeter reading. After applying the zero correction it was also necessary to correct the "invert" reading for the additional dilution entailed by taking 6.5 ml. of the "direct" solution /

solution and making it up to 7 mls. after inversion. Both these corrections have been applied to the figures shown. Since every solution analysed was sampled with same 0.5 ml. pipette and measured in the same 7 ml. flask, all the readings given are strictly comparable and refer to the diluted solutions. *e.g.*:-

Results

Initial Concentrations :-

Sucrose 1 M
Glucose 1 M

Time	Direct Reading(D)	Invert Reading(I)	Change in rotation D - I	Factor by which [sucrose] has increased	Calculated original rotation of the sucrose	Rotation due to glucose	Factor by which [glucose] has increased
0	2.31	0.19	2.12	1.00	1.69	0.62	1.00
2	2.32	0.19	2.13	1.00	1.69	0.63	1.02
5	2.32	0.19	2.13	1.00	1.69	0.63	1.02
10	2.39	0.20	2.19	1.03	1.74	0.65	1.05
20	2.41	0.22	2.19	1.03	1.74	0.67	1.08
30	2.45	0.22	2.23	1.05	1.77	0.68	1.10
115	2.51	0.23	2.28	1.08	1.78	0.68	1.10

Notes.

(1) It is to be noted that these experiments were carried out only to see if the rate of concentration of one species was different from that of another. All that was then required was the factor by which the concentration /

concentration of each component had increased in a given time. If the factors were the same, no separation had occurred.

(2) It will be seen that the solution used in the above experiment contained 34.2 g. of sucrose and 18.0 g. of glucose in 100 mls. of solution. It was found necessary to keep the total solids dissolved in 100 mls. below 55 g., for otherwise the solution was too viscous to enable 0.5 ml. to be withdrawn in a reproducible manner.

(3) The one constant required in the above determination is the rotation of 1.00 M sucrose in the original solution. This was obtained from a separate determination, the value 1.69° used above being obtained.

Analysis of Solutions containing Sucrose and Glycerol.

The method used was based on that of Fulmer, Hickey and Underkofler,[66] which involves the determination of glucose by the copper titration method of Shaffer and Somogyi[67] followed by the oxidation of another sample with ceric sulphate under standardised conditions. Both the sugar and the glycerol are oxidised, but, applying a correction for the ceric sulphate used by the sugar, the glycerol may be calculated. In order to adapt the method to the analysis of sucrose, the sucrose was first of all inverted. Since Shaffer and Somogyi /

Somogyi have also used the copper titration method for the estimation of fructose, there seemed to be no reason why this modification should not work; and such was found to be the case.

Preparation of Mixtures. The glycerol used was the purest obtainable, but as investigation of the literature showed that glycerol is only freed from traces of water with considerable difficulty and furthermore is extremely hygroscopic, the solutions were prepared as follows. A solution of approximately twice the concentration required was prepared and its specific gravity determined. Reference to published tables then gave the actual concentration. A suitable volume of this solution was then taken and in it was dissolved the required amount of sucrose and the solution made up to 100 mls. in a graduated flask.

Dilution of solution prior to analysis.

A sample of about 10 drops was withdrawn from the column and of it a 0.5 ml. portion was taken and placed in an inversion tube with 0.5 ml. of 9N H_2SO_4 (HCl cannot be used, for it is oxidised by ceric sulphate which is used later on). A rapid jet of water from a wash bottle was then used both to stir up and dilute the mixture to the 7 ml. mark. (This mixing is important, for if it is not carried out the sugar chars on heating) The diluted solution was then heated at 70°C. in the bath for 30 minutes as described above. The contents of /

of the tube were then washed into a 100 ml. graduated flask and made up to the mark. Portions of this solution are used for the Ceric oxidation (vide infra). For the Fehling's determination, 10 mls. of the solution were further diluted to 100 mls.

Determination of the Sucrose.

The method is a volumetric adaptation of the Fehling's method. The reducing sugar is oxidised by an alkaline cupric tartrate solution with the production of Cu_2O. Also present in the solution are definite amounts of KI and KIO_3 and upon acidification these interact to produce iodine which re-oxidises the Cu_2O. The unused iodine is then titrated with $Na_2S_2O_3$ solution and the difference between this titration and that of a control determination is proportional to the reducing sugar present.

Preparation of the reagent.

25 g Na_2CO_3 (anhydrous)	200 g Na_2SO_4 (anhyd. A.R.)
25 g Rochelle Salt	1.5g KI
4 g $CuSO_4.5H_2O$	6 ml. of N.KIO_3

The sodium carbonate and Rochelle salt are dissolved in about 800 ml. of water; then 40 ml. of 10% copper sulphate solution are introduced below the surface of the solution with stirring. This is followed by the addition of the bicarbonate, sulphate and iodide. The solution is heated to boiling, kept boiling for about /

about 30 seconds, cooled, and after addition of the KIO_3, diluted to 1 litre. It is then set aside for 2-3 days in order to permit impurities to flocculate, and filtered. In the present work it was found that, after setting aside, a large proportion of the sodium sulphate had come out of solution as $Na_2SO_4.10H_2O$ due to the low temperature at the time when the work was being done. The function of the Na_2SO_4 is to reduce the solubility of oxygen in the reagent and thus it is not vital, so the solution was decanted off the crystals through a filter and stored in the dark in a Pyrex bottle.

Method:- To 2 mls. of the twice diluted solution in a pyrex boiling tube (25 x 200 mm.) was added 5 mls. of the reagent and the sides of the tube washed down with 3 mls. of distilled water. The contents were then well mixed by rotation and the tube, covered by a glass bulb, was placed in a boiling water bath for 35 mins. in such a position that 100 mm. was immersed. The tube was then transferred to a cold water bath (at $10^{\circ}C.$) for not more than 2 minutes, thus bringing the temperature to about $30^{\circ}C.$ as desired, and 5 mls. of N. H_2SO_4 added and the solution well mixed. It was then allowed to stand with occasional shaking for 15-20 mins. or until all the CuI had dissolved (important), when it was immediately titrated with 0.05 N. $Na_2S_2O_3$ (freshly diluted from N/10 which was stabilised by 0.2 g/litre Na_2CO_3) /.

Na_2CO_3) using 1 ml. of 1% starch solution at the end-point. A control determination was also performed and the difference between the two titrations gave the amount of iodine used by the sugar.

Ceric Oxidation.

Reagent: 0.1 N Ceric sulphate in 1.6 N sulphuric acid

After the solution had been diluted once (vide supra) a 2 ml. sample was withdrawn and placed in a (200 x 25 mm.) pyrex boiling tube. To this was added 5 mls. of reagent and 2 mls. of 1:1 sulphuric acid, and the sides washed down with 3 mls. of distilled water, and the contents well mixed. The tube, covered by a glass bulb, was then heated half-immersed in a boiling water bath for one hour, after which it was cooled to about 20°C. by immersing in a cold water bath for 5-10 minutes. When cool it was titrated with 0.1 N ferrous ammonium sulphate, using 1 drop of ortho-phenanthroline ferrous sulphate complex as indicator which gave an excellent end-point. A control determination was also carried out and the difference between the two titrations was a measure of the ceric sulphate used by the glycerol and inverted sucrose. e.g.:-

Results.

1. Three solutions of known composition were prepared.

No. /

No.	Sucrose	Glycerol	Sucrose + Glycerol
1	30.67 g/100 ml.	8.965 g/100 ml.	39.64 g/100 ml.
2	33.73 "	9.862 "	43.59 "
3	36.80 "	9.862 "	46.66 "

2. Determination of sucrose.

After dilution, 2 ml. of sample No. 1 will contain

$$\left(2 \times \frac{0.5}{100} \times \frac{10}{100} \times \frac{1000}{100} \times 30.67\right) \text{ mg. sucrose}$$

$$= 0.3067 \text{ mg.}$$

Similarly 2 ml. of sample No. 2 will contain 0.3373 mg.

" 2 " " " No. 3 " " 0.3680 mg.

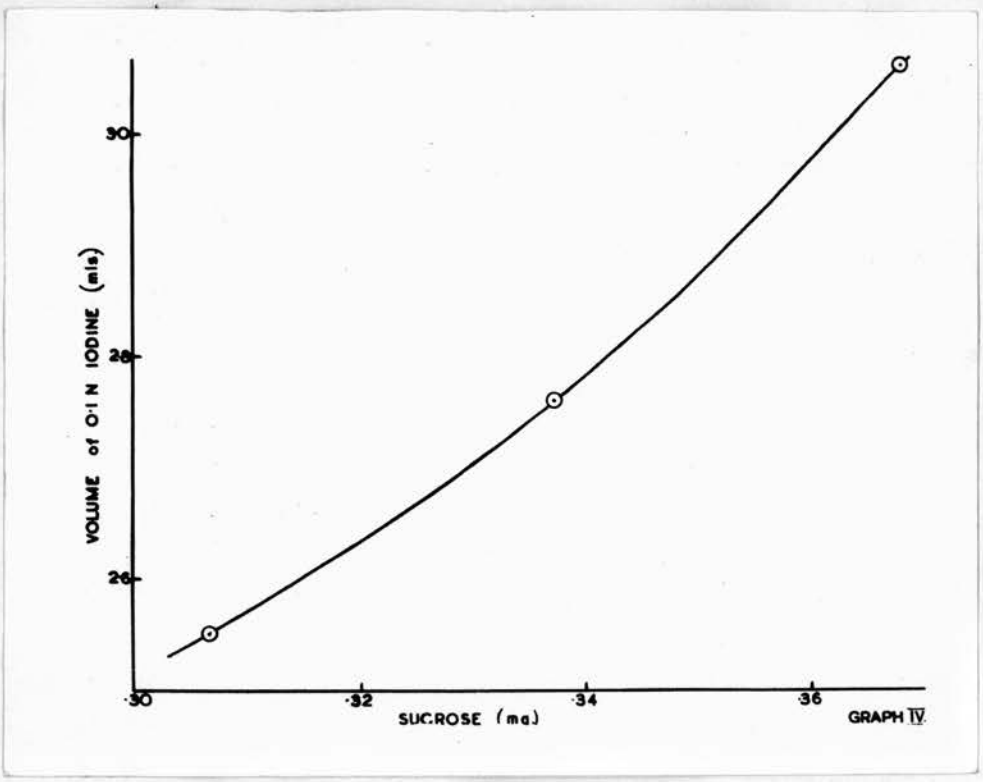
		Average
2 ml. sample 1 + reagents used of 0.05 N $Na_2S_2O_3$		
	(3.28; 3.21; 3.25)	3.25 ml.
" " 2 + " "	(3.03; 3.03; 3.07)	3.04 "
" " 3 + " "	(2.85; 2.73; 2.63)	2.74 "
Blank determination (average of 15 determinations)		5.80 "

Thus 0.3067 mg. Sucrose used 2.55 ml. of 0.05 N Iodine

0.3373 mg. " " 2.76 ml. " " "

0.3680 mg. " " 3.06 ml. " " "

These results were incorporated in Graph IV



Solution No. 1 was now diffused for 30 minutes and a sample taken.

2 ml. of sample after the customary dilutionsused of 0.05 N thiosulphate

2.82; 2.75; 2.63; 2.65; 2.70; 2.66 Aver. 2.67 mls.

i.e., sample used 3.13 mls. of 0.05 N Iodine

∴ From Graph IV, sample contained 0.374 mg. sucrose

∴ Sample withdrawn from column contained 37.4 g. sucrose/100 ml. Thus the concentration of the sucrose had been increased in the ratio $\frac{37.4}{30.67} = 1.22$

3. /

3. Determination of Sucrose + Glycerol

After dilution, 2 ml. of sample No. 1 will contain

$$\left(2 \times \frac{0.5}{100} \times \frac{1}{100} \times \frac{1000}{1} \times 39.64\right) = 3.964 \text{ mg. solids}$$

Similarly 2 ml. of sample No. 2 will contain 4.359 " "

" 2 " " No. 3 " " 4.666 " "

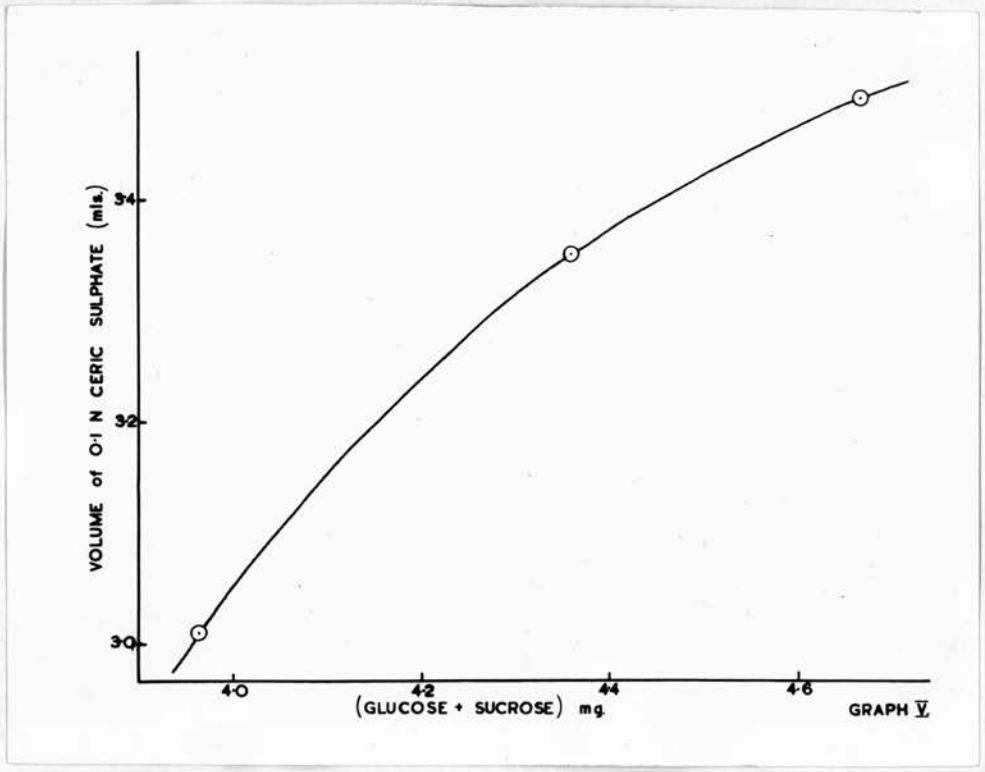
2 ml. sample 1 + reagents used of 0.1 N Fe^{++}		Average
	(1.77; 1.77)	1.77 mls.
" " 2 + " " " "	(1.42; 1.44)	1.43 "
" " 3 + " " " "	(1.29; 1.28)	1.29 "
Blank determination (no variation)		4.78 "

Thus 3.964 mg. used 3.01 mls. of 0.1N ceric sulphate

4.359 mg. " 3.35 mls. " " "

4.666 mg. " 3.49 mls. " " "

These results were incorporated in Graph V.



Solution No. 1 was now diffused for 30 minutes and a sample taken.

2 ml. of sample after customary dilution used of 0.1 N Ferrous 1.20; 1.22; Average 1.21 mls.

i.e., sample used 3.57 mls. of 0.1 N ceric sulphate

∴ From Graph V sample contained 4.780 mg. of sucrose + glycerol

∴ Sample from column contained 47.8 g. of sucrose + glycerol/100 ml.

But of this 37.4 g. was sucrose

∴ 10.4 g. was glycerol

Thus /

Thus the concentration of the glycerol had been increased by the factor $\frac{10.4}{8.965} = 1.16$.

Note 1. The Fehling's determination appeared to be particularly sensitive to oxidation by the air. Hence the attempt to increase the accuracy by a large number of determinations.

2. The method of calculation is on the same lines as that given by Fulmer, Hickey and Underkofler, who examined this estimation in some detail. It differs, however, in that instead of using the known samples to obtain the values of the constants in a logarithmic equation given by them, a graphical method is used. Both methods were found to be equally good

Analysis of Solutions of acetone + glycerol.

Acetone. The acetone was determined by the alkaline hypoiodite method described above. It was fortunate that the glycerol did not interfere with this determination. (This is shown in graph VI.) The solution as withdrawn from the column was diluted 0.5 mls. ⟶ 50 mls. and the amount of this solution used for analysis is indicated in the table.

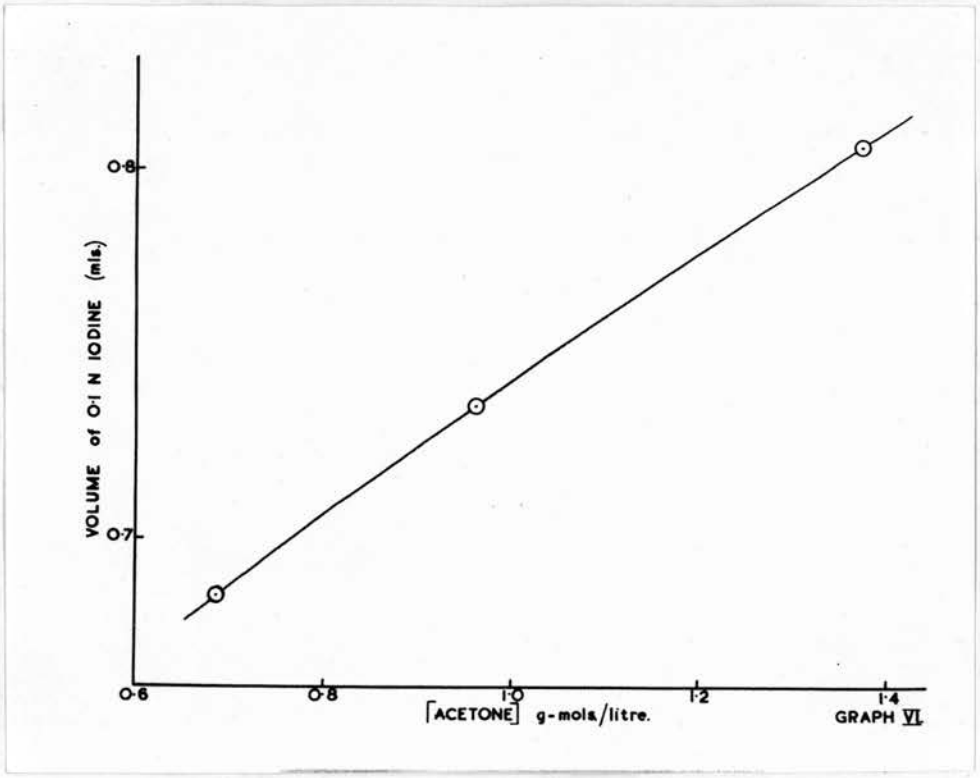
Glycerol. As is shown by the control determinations recorded below (see Graph VII) it appears that ceric sulphate /

sulphate will oxidise acetone quantitatively under standard conditions just as it will oxidise glycerol. The oxidation was accordingly carried out exactly as described for glycerol. The volume of the 0.5 ml. → 50 mls. diluted solution used is given in the table. Determination of acetone+glycerol by this method and separate determination of the acetone (vide supra) gave the concentration of the glycerol. *e.g.*:-

Results.

Sample	[Glycerol] g/100 ml	[Acetone] ml/ 100 ml.	[Acetone] g/mol. litre	Vol. of diluted sample used for analysis	Vol. of 0.1 N I_2 used by sample	Vol. I_2 per 0.01 ml. of original soln.
A	24.25	5.00	0.6869	20 mls.	13.69	0.6845
B	27.28	7.00	0.9616	20 "	14.72	0.7360
C	15.16	10.00	1.3744	14 "	11.29	0.8064

The last column gives the volume (obtained by proportion) of 0.1 N Iodine which would have been used by 0.01 ml. of the original. These figures are plotted against the molecular concentration of acetone in Graph VI.



Samples B and C were now diffused for 10 minutes.

20 mls. of B after diffusion used 14.59 mls. of I_2

$\equiv$ 0.7295 mls. per 0.01 ml. of original solution

14 mls. of C after diffusion used 11.07 mls. of I_2

$\equiv$ 0.7907 mls. per 0.01 ml. of original solution.

Referring to graph and correcting for dilution:-

B after diffusion contained 0.935 g-mol/litre of acetone

C " " " 1.262 " / " " "

i.e., B lost 0.027 g-mol/litre acetone

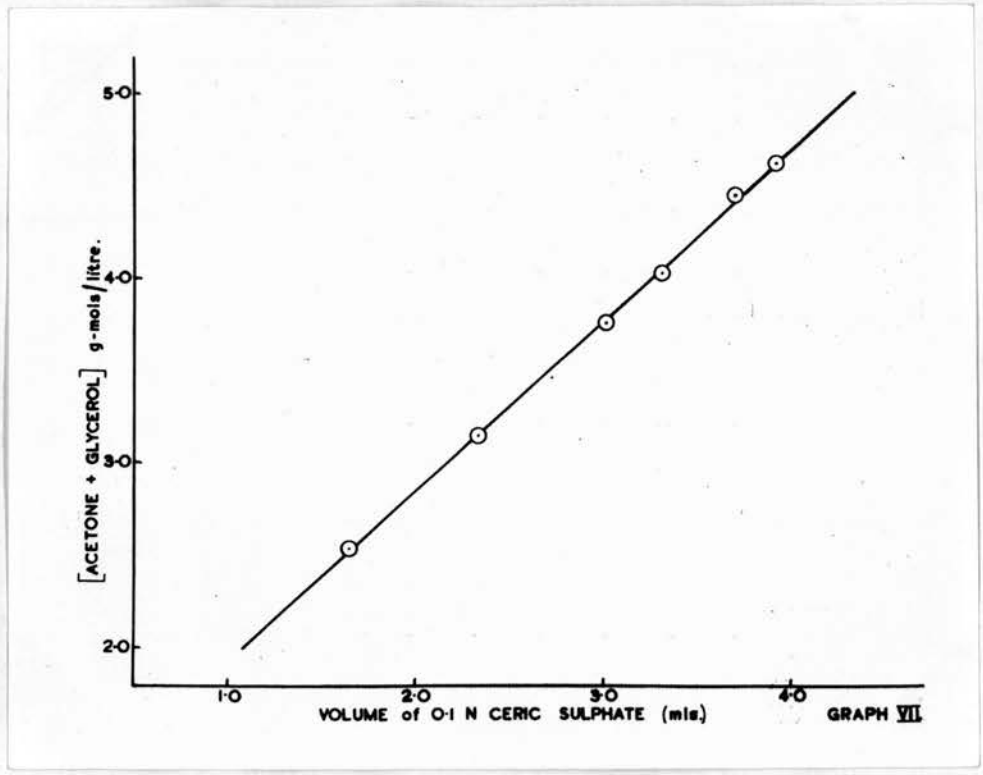
C " 0.112 " " "

Results /

Results. Acetone + Glycerol.

Sample	[Acetone] (ml/100ml)	[Glycerol] (g./100ml.)	[Acetone] g-mol/litre	[Glycerol] g-mol/litre	Total mole.conc.	Vol. of diluted solution used for analysis (mls.)	Vol. of ceric used (mls.)	Vol. per 0.01 ml. original solution (mls.)
D	nil	15.16	nil	1.648	1.648	3.05	7.75	2.541
E	5.00	15.16	0.6869	1.648	2.335	2.25	7.68	3.147
F	5.00	24.25	0.6869	2.636	3.323	1.60	4.03	4.030
B	7.00	27.28	0.9616	2.965	3.927	1.60	4.62	4.620
C	10.00	15.16	1.374	1.648	3.022	1.80	6.77	3.761
G	15.00	15.16	2.060	1.648	3.708	1.50	6.68	4.453

The last column giving the proportional volume per 0.01 ml. of original solution. These figures are plotted against total molecular concentration in Graph VII.



GRAPH VII

Unknown samples.

1 ml. of sample B after diffusion used 4.75 mls. 0.1 N ceric sulphate ≡ 4.75 mls. per 0.01 ml. of original soln.

1.80 ml. of sample C after diffusion used 6.63 ml. 0.1 N ceric sulphate ≡ 3.684 mls. per 0.01 ml. of original soln.

Referring to the graph and correcting for dilution:-

B after diffusion contained 4.05 g-mol/litre (acetone + glycerol)

C " " " 2.95 " "

Thus /

Thus B gained by diffusion 0.12 moles (acetone + glycerol), but since 0.027 moles of acetone were lost this corresponds to a gain of 0.147 moles of glycerol.

i.e., Sample B Glycerol:- gained 0.147 g-mol./litre
Acetone :- lost 0.027 g-mol./litre

Similarly C had a net loss of 0.07 g-mol./litre but since 0.112 g-mols. of acetone were lost this corresponds to a gain of 0.042 g-mol./litre of glycerol,

i.e., Sample C Glycerol:- gained 0.042 g-mol./litre
Acetone :- lost 0.112 g-mol./litre

Experiments on the Soret Effect.

The ends of a piece of thin walled soft glass tubing of 1.2 cm. external diameter were drawn out so that the distance between the shoulders where narrowing commenced was 11 cm. One end was then sealed, and the solution to be examined introduced through the other by means of a vacuum. The tube was then placed in a water bath, the temperature of which was the mean of the two temperatures to be employed in the experiment: and when it had heated up, the open end was sealed with a blowpipe flame. This tube was now held vertically by rubber stoppers in two short condenser jackets, as shown in fig. A

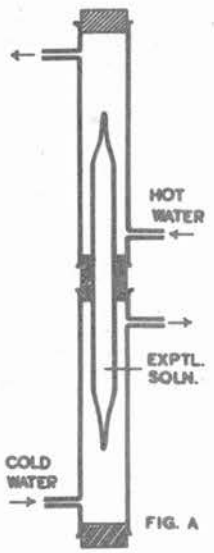


FIG. A

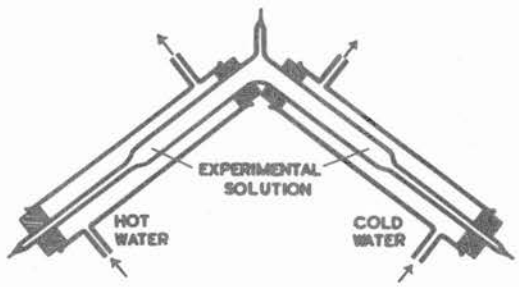


FIG. B.

Hot water was then passed through the upper jacket and cold water through the lower one; and after the solution had diffused for the required time, the tube was removed and, still keeping it vertical, the upper seal was broken and replaced by a short piece of rubber tubing and a pinch clip. The lower seal was then broken and by use of the clip the solution was run out in three portions, which were analysed. This arrangement was used principally for solutions of strong acids and the acid concentration was determined by titration of small portions with standard sodium hydroxide.

Example. Experiment using 1.12 N HCl. Duration 7 hr.
Hot side - Steam: Cold side - Water at 5°C.

Analysis: (NaOH = 1.000 N)

0.5 ml. original solution used 5.60 mls. of NaOH
0.5 ml. upper portion aft. diffusion used 5.34 mls. of NaOH
0.5 ml. centre " " " " 5.60 ml. of NaOH
0.5 ml. lower " " " " 5.84 ml. of NaOH

	g.equivs./litre
[HCl] in original soln. (& also centre portion)	1.120
[HCl] conc. in upper portion after diffusion	1.068
[HCl] conc. in lower " " "	1.168

Thus /

Thus:- increase in concentration in lower region 0.048 g.equivs./litre. This figure is compared, in the discussion, with the result obtained by effecting the thermal diffusion of this same solution in the column, i.e., with convection.

The apparatus B which had approximately the same dimensions was also used. The ends of this tube projected out of the stoppers as shown, and by means of another tube at the top of the inverted V it was possible to empty each leg of the V without disturbing the experimental arrangement. This apparatus was used for acetone solutions and the direction of the small concentration change was observed by means of a Zeiss Interferometer, which was used qualitatively only.

RESULTS AND DISCUSSION

Introduction.

It will already have been appreciated that the main difference between this work and that which has preceded it in the study of convective thermal diffusion in liquids lies in the fact that previous workers have dealt with the equilibrium separation whereas we are here concerned with the initial rate of the process. While this is certainly true in the case of the practical work which has been done, it is none the less true on the theoretical side. However, some comparison is possible in that it does appear that a set of experimental conditions which would give rise to a large equilibrium separation also give rise to a large initial rate of separation.

P. Debye [55], in his theoretical paper regards the apparatus as consisting of two vertical parallel plates having a temperature difference of τ °C. between them, at a distance apart "a" and of height "h" and of a breadth so great compared with "a" that alterations in this direction may be neglected. (A circular column may be expected to behave similarly - to a first approximation at least.) He then proceeds to find what value of "a" should give a maximum separation for assumed /

assumed values of τ, h, etc., obtaining

$$a^3 = \frac{600\,\eta D}{\beta \rho g \tau}$$

where η is the viscosity, D the coefficient of diffusion, β the coefficient of cubical expansion, ρ the density (each of the solution used) and g is the acceleration of gravity. Thus in C.G.S. units, taking as mean values $\eta = 0.01$, $D = 10^{-5}$, $\beta = 0.001$, $g = 1000$, $\rho = 1$ and $\tau = 90^{\circ}C$.

$$a \fallingdotseq 0.1 \text{ mm.}$$

No results are recorded in the literature for a reduction in the separation at very small values of "a"; in fact, the value of $a \fallingdotseq 0.1$ mm. is smaller than that feasible in any simple experimental arrangement, and in general the smaller the experimental distance apart of the plates the greater is the separation. This is not, however, always desirable since there is a corresponding decrease in the amount of material in the column, and the withdrawal of a small portion for analysis causes a proportionately greater disturbing effect, and in practice a balance has to be struck between the two. The value for the column used ($\fallingdotseq 0.7$ mm.) was found quite suitable.

The Length of the Column. The closest approach which Debye makes to the consideration of the initial rate of the /

the process is in the evaluation of the separation obtained in a time "much shorter than that required to reach equilibrium." In this connection he considers two cases -

(i) where the heated (or "working") volume "A" is very much greater than the volume of the "reservoir" "V" where the "reservoir" comprises all liquid not subject to the gradient, i.e., $\frac{V}{A} \ll 1$

(ii) where there is a large reservoir, i.e.,

$$\frac{V}{A} \gg 1$$

The column used in the present series of experiments falls into the first category and for this case the expression obtained is

$$\frac{n_o}{n_u} = 1 - 1{\cdot}4 \frac{D_T \tau}{a\sqrt{D}} \cdot \sqrt{t}$$

where n_o is the concentration at the top of the column, n_u the concentration at the foot, D_T the coefficient of thermal diffusion, "t" the time and the other terms have the same significance as previously. This expression is notable in that the height of the column does not enter into it, i.e., the separation is independent of the height of the column. However, this expression, strictly speaking, holds only for the value of "a" which will give a maximum separation, as described above, and accordingly it appeared desirable to see whether it would hold for the "a" used experimentally. In order to test this point the following experiments /

experiments were carried out.

A burette was attached to the tap at the foot of the column as has been described above, and from it a solution of 30 g./100 mls. of glucose was run into the column up to the level of the top of the upper stopper. The heating and cooling system was then turned on and the column allowed to operate for 30 mins. A sample from the foot of the column was then analysed by the refractometer. This solution was then removed and, after cleaning and drying, the column was filled with fresh solution, to the top of the upper stopper once more. Then a known volume was run out again into the burette and the remaining column of liquid diffused. A series of such determinations were carried out and assuming that the length of the liquid column was proportional to the volume of liquid in the column, it was possible to graph change produced for various lengths of solution, which, for liquids, is the same thing as various lengths of column.

Results.

Solution used:- Glucose, 1.726 g-mol./litre.
Volume of solution filling heated space of length 128 cm. = 28.20 mls.

First /

First Series.

Heating :- Steam at 100°C. { Gradient 95°C.
Cooling :- Water at 5°C. { Mean Temperature 53°C.

Expt. No.	Vol. of Solution withdrawn (mls.)	Length of Liquid Column (cm.)	Final [Glucose] at foot of column (g-mol./litre)	[Glucose] change in 30 mins. (g-mol./litre)
1	nil	128.0	1.902	0.176
2	2.00	119.0	1.902	0.176
3	5.00	105.0	1.902	0.176
4	8.00	91.7	1.898	0.172
5	11.00	78.1	1.878	0.152
6	14.00	64.5	1.873	0.147
7	17.00	50.8	1.869	0.143
8	20.00	37.3	1.840	0.114
9	22.00	28.2	1.826	0.100

Second Series.

Heating :- Steam at 100°C. { Gradient 51°C.
Cooling :- Water at 49°C. { Mean Temperature 75°C.

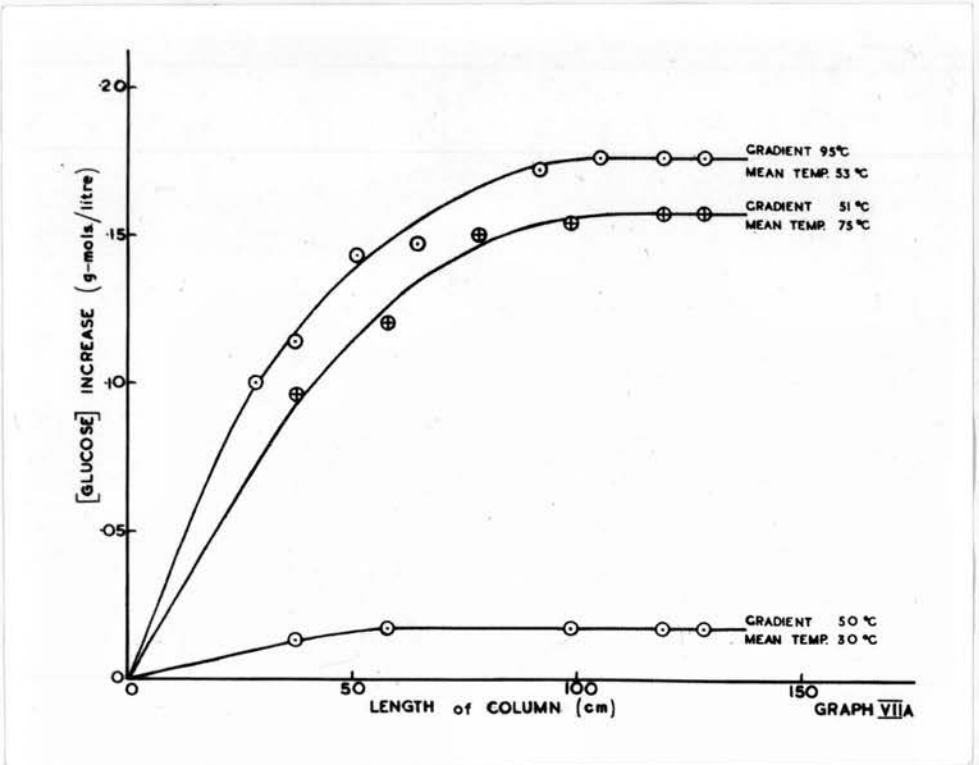
Expt. No.	Vol. of Solution withdrawn (mls.)	Length of Liquid Column (cm.)	Final [Glucose] at foot of column (g-mol./litre)	[Glucose] change in 30 mins. (g-mol./litre)
10	nil	128.0	1.883	0.157
11	2.00	119.0	1.883	0.157
12	6.50	98.6	1.880	0.154
13	11.00	78.1	1.876	0.150
14	15.50	57.7	1.847	0.120
15	20.00	37.3	1.822	0.096

Third Series.

Heating :- Water at 55°C. } Gradient 50°C.
Cooling :- Water at 5°C. } Mean Temperature 30°C.

Expt. No.	Vol. of Solution withdrawn (mls.)	Length of Liquid Column (cm.)	Final [Glucose] at foot of column (g-mol./litre)	[Glucose] change in 30 mins. (g-mol./litre)
16	nil	128.0	1.743	0.017
17	2.00	119.0	1.743	0.017
18	6.50	98.6	1.743	0.017
19	16.00	57.7	1.743	0.017
20	20.00	37.3	1.739	0.013

The second and fourth columns of each table are plotted in Graph VIIA



These results show that for the larger gradients and higher mean temperatures the separation is independent of the length when the column is almost full. For smaller gradients and lower mean temperatures the separation is independent of the length over a much greater range. The temperatures used in these experiments were chosen in such a way as to test this particular point at the limit of the experimental conditions. In no case in the later experiments is a gradient greater than 95°C. used, and in few cases only is the mean temperature higher than 75°C., and even then not much higher.

Thus under the conditions of working in the main series of experiments the separation will not be directly affected by the reduction in the length of the column due to the withdrawal of samples for analysis. The actual removal, then, is the only disturbing feature, and, as has already been mentioned, this is kept as small as possible by making the portions withdrawn small.

In addition, all experiments are strictly comparable with each other in that they lie in a region for which the length of the column is immaterial - which is a great simplification.

Theoretical /

Theoretical Treatment.

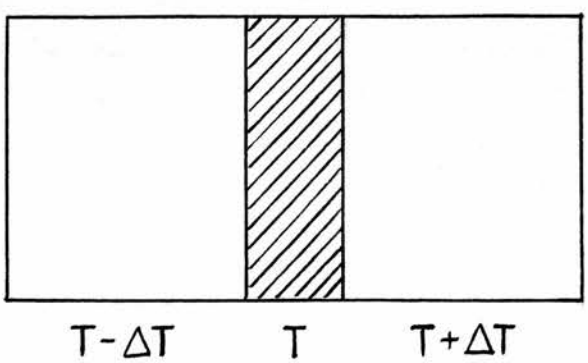
It was desired to have some simple, even if only approximate, theory to which the experimental results might be related.

The procedure adopted was to derive a theory for the gaseous process first, because there is a great variety of experimental data with which such a theory can be compared. Then, having obtained a theory which reproduced the main features of gaseous thermal diffusion, the same general principles were applied to the liquid system.

It is desired to emphasise that the theory is intended to be approximate only: keeping this in mind, the considerable measure of agreement between the calculated and observed results may be taken to show that the method of approach is correct in its essentials.

Section I: A Simple Theory for Thermal Diffusion in Gases.

Consider a mixture of two gases in a narrow cell of constant volume the ends of which are maintained at temperatures $T-\Delta T$ and $T+\Delta T$ the narrow central strip being at T.



It is observed that the concentration of one species increases in one region and decreases in the other, and vice versa for the other species.

On simple kinetic theory there is no explanation for this phenomenon. For, a molecule of one species will diffuse from the T region to, say, the $T+\Delta T$ region at a rate determined by the condition of concentration, molecular diameter, mass, etc. At the same time the reverse process may be visualised as taking place to an equal extent: since the conditions along the path of transfer are the same, no net change in concentration should occur. This will apply to the other type of molecule of the binary mixture, although the actual path traversed in unit time would be different from that of the first. No relative concentration gradient is therefore to be expected, because, essentially the conditions encountered in the path between the two temperature regions are regarded as the same, no matter the direction of the transfer.

It has become apparent that the explanation of the phenomenon lies in the fact that a molecule from the $T+\Delta T$ region on entering the T region does not at once lost the characteristics which it possessed as a $T+\Delta T$ molecule, the effect in general being described as a "persistence of velocity" effect. Applying this principle to the above system, if a molecule from the T region is regarded as "projected" into the $T+\Delta T$ region, the /

the reverse projection of a $T+\Delta T$ molecule will not exactly restore the original situation, because the diffusional characteristics are not now the same throughout the path of travel. A relative concentration change will then occur which, since the total pressure in the cell remains the same, must be balanced by a mass-mechanical movement of the whole binary mixture in the opposite direction. This conception, simplified so as to bring out the main essential features, is taken as the basis of the following treatment, applied in the first instance to a binary gas mixture.

Gas System.

For the diffusion of a particle A through a gas X at concentration $[X]$, the rate of diffusion at a temperature T may be taken as $\frac{D_x^A}{[X]}$ where D_x^A is a diffusion constant containing molecular weight and diameter factors only. If the A particles are of concentration $[A]$ the number of A molecules diffusing in a given direction in unit time will be $[A]\frac{D_x^A}{[X]}$

Where the A particles diffuse through a binary mixture of X_1 and X_2 molecules, the time taken to diffuse a given distance in the mixture may be taken as the sum of the times for the constituents considered singly. Thus for one A particle

$$\frac{1}{D^A_{X_1X_2}} = \frac{[X_1]}{D^A_{X_1}} + \frac{[X_2]}{D^A_{X_2}}$$

and hence

$$D^A_{X_1X_2} = \left[\frac{[X_1]}{D^A_{X_1}} + \frac{[X_2]}{D^A_{X_2}}\right]^{-1}$$

Let the binary gas mixture be represented by two different molecules of mass M_1 and M_2 and of diameter σ_1 and σ_2 and of concentration x_1 and x_2 at temperature T. Since the total gas pressure remains constant, the corresponding concentrations at $T+\Delta T$ and $T-\Delta T$ will be

$$x_1 \cdot \frac{T}{T+\Delta T} \quad , \quad x_2 \cdot \frac{T}{T+\Delta T} \quad \text{and} \quad x_1 \cdot \frac{T}{T-\Delta T} \quad , \quad x_2 \cdot \frac{T}{T-\Delta T}$$

Applying the above formula, the number of M_1 molecules passing :-

(a) from T to $T+\Delta T$ will be

$$\Delta x_1 = x_1 \left[\frac{x_1 T}{(T+\Delta T) D_{x_1}^{x_1}} + \frac{x_2 T}{(T+\Delta T) D_{x_2}^{x_1}} \right]^{-1}$$

$$= x_1 \frac{T+\Delta T}{T} \left[\frac{x_1}{D_{x_1}^{x_1}} + \frac{x_2}{D_{x_2}^{x_1}} \right]^{-1}$$

$$= x_1 \frac{T+\Delta T}{T} \cdot D_{x_1 x_2}^{x_1}$$

(b) from T to $T-\Delta T$ similarly $\Delta x_1' = x_1 \frac{T-\Delta T}{T} D_{x_1 x_2}^{x_1}$

Similar expressions will hold for M_2

This flow must be balanced by a movement of the whole mass of binary gas mixture in the reverse direction where now the relative numbers of M_1 and M_2 molecules will be determined by the relative concentrations of /

of M_1 and M_2, i.e., $\frac{x_1}{x_1+x_2}$ and $\frac{x_2}{x_1+x_2}$

Consider, first, the number of M_1 molecules thus moving:-

(a) from $T+\Delta T \rightarrow T$ (i) due to Δx_1 moving $T \rightarrow T+\Delta T$

$$= \Delta x_1 \frac{x_1}{x_1+x_2}$$

(ii) due to Δx_2 moving $T \rightarrow T+\Delta T$

$$= \Delta x_2 \frac{x_1}{x_1+x_2}$$

(b) from $T-\Delta T \rightarrow T$ (i) due to $\Delta x_1'$ moving $T \rightarrow T-\Delta T$

$$= \Delta x_1' \frac{x_1}{x_1+x_2}$$

(ii) due to $\Delta x_2'$ moving $T \rightarrow T-\Delta T$

$$= \Delta x_2' \frac{x_1}{x_1+x_2}$$

Similar expressions will hold for M_2 in this case also.

Finally, excess of M_1 over M_2 molecules moving from $T-\Delta T$ to T to $T+\Delta T$:-

$$\Delta S = \frac{2x_2}{x_1+x_2}\left(\Delta x_1 - \Delta x_1'\right) - \frac{2x_1}{x_1+x_2}\left(\Delta x_2 - \Delta x_2'\right)$$

Substituting the values given above for the Δx_1, Δx_2, etc.

$$\Delta S = \frac{4x_1x_2}{x_1+x_2} \cdot \frac{\Delta T}{T}\left(D_{x_1x_2}^{x_1} - D_{x_1x_2}^{x_2}\right)$$

If the D terms are regarded as temperature independent over a short temperature range, we have an integration

$$S \propto \frac{x_1 x_2}{x_1 + x_2}\left(D^{x_1}_{x_1 x_2} - D^{x_2}_{x_1 x_2}\right) \log T$$

It will be observed that in the above treatment, separation is essentially due to the fact that the diffusion is inversely proportional to the concentration, which is, in its turn, controlled in relation to temperature by the simple gas law. It is therefore necessary to enquire if such a simple formulation does indeed indicate the essential features of thermal duffusion in gases. It is first of all necessary to evaluate the D factors in terms of known quantities.

The coefficient of diffusion of a particle A through a gas X will depend mainly on the respective masses and diameters. By simple kinetic theory as applied to rigid molecules this coefficient may be taken as

$$D^{A}_{X} \propto \frac{\sqrt{\frac{1}{M_A} + \frac{1}{M_X}}}{\sigma^2_{AX}}$$

where M_A and M_X are the respective masses and σ_{AX} is the sum of the radii. In the present case

$$D^{x_1}_{x_1 x_2} = \left[\frac{x_1}{D^{x_1}_{x_1}} + \frac{x_2}{D^{x_1}_{x_2}}\right]^{-1} \propto \left[\frac{\sigma^2_{1.1}\, x_1}{\sqrt{\frac{1}{M_1} + \frac{1}{M_1}}} + \frac{\sigma^2_{1.2}\, x_2}{\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}\right]^{-1}$$

$$\left(D^{x_2}_{x_1 x_2} \text{ similarly}\right)$$

where $\sigma_{1\cdot2}$ etc. represent the sum of the radii of the colliding molecules.

Inserting these values into the expression for S given above we obtain

$$S \propto \frac{x_1 x_2}{x_1 + x_2} \log T \left\{ \left[\frac{\sigma_{1\cdot1}^2 x_1}{\sqrt{\frac{1}{M_1}+\frac{1}{M_1}}} + \frac{\sigma_{1\cdot2}^2 x_2}{\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}} \right]^{-1} - \left[\frac{\sigma_{2\cdot1}^2 x_1}{\sqrt{\frac{1}{M_2}+\frac{1}{M_1}}} + \frac{\sigma_{2\cdot2}^2 x_2}{\sqrt{\frac{1}{M_2}+\frac{1}{M_2}}} \right]^{-1} \right\}$$

Strictly speaking, this refers to the separation in a small time interval, but as the simple thermal diffusion effect is very small, the values of x_1 & x_2 at equilibrium will differ little from the values at time zero, and this expression may be taken to give the equilibrium separation; this is supported by the following considerations.

The expression brings out the essential features of thermal diffusion as follows:-

1. Dependence on concentration.

No separation is, of course, obtained if x_1 or x_2 is zero and there must be at least one value of x_1 and x_2 for which the separation will be a maximum. This will not necessarily occur at $x_1 = x_2$ for these are concentration factors in the last term also.

2. Dependence on the molecular weight.

If the diameters of the gas molecules be assumed equal, then for any given concentration the sign of the separation will depend on the relative magnitudes of the molecular weights. Thus if we take $x_1 = x_2 = 0{\cdot}5$ and $\sigma_{1\cdot1} = \sigma_{1\cdot2} = \sigma_{2\cdot1} = \sigma_{2\cdot2} = \sigma$,

the expression reduces to

$$S \propto \frac{\log T}{\sigma^2\sqrt{2}}\left[\frac{\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}\left(\sqrt{M_2}-\sqrt{M_1}\right)}{\sqrt{M_1M_2}\left(\sqrt{\frac{2}{M_1}}+\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}\right)\left(\sqrt{\frac{2}{M_2}}+\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}\right)}\right]$$

and thus the sign of the separation depends on the relative magnitudes of M_1 and M_2.

3. Dependence on the diameter.

If we put in this case $x_1 = x_2 = 0.5$ and $M_1 = M_2 = 0.5$ we obtain a similar expression in which all the factors are always positive except $\sigma_{2\cdot2} - \sigma_{1\cdot1}$ and accordingly the relative diameters determine the sign of the separation.

4. Dependence on the temperature.

The logarithmic dependence on the temperature is entirely as expected and in complete agreement with the rigorous expression derived by Chapman & Cowling,[25] or by Fürth.[27]

That the above simple theory does indicate the essential features of gaseous thermal diffusion is readily confirmed by comparison with the published results

Further aspects of the theory will be given later: for the present the main conceptions are now applied to thermal diffusion in liquids.

Section /

Section II: A Simple Theory for Thermal Diffusion in Liquids.

As has been pointed out in the introduction, the adaptation of a theory designed for a gas system to a liquid has not, in the past, been particularly successful. However it is considered that in the case of Thermal Diffusion the main essential features must be at least similar in the two cases. For example, it is to be expected that the separation in the case of liquids will be related to the temperature difference and the molecular masses and diameters.

In applying the principles of gas diffusion theory to the corresponding case of liquids it is necessary to obtain an expression for the rate of diffusion of a molecule through a liquid medium. For large sized or "macroscopic" particles, e.g., gold sol particles, Stokes Law has been shown to apply.

$$\text{i.e. } D \propto \frac{1}{3\pi\eta d}$$

where η is the viscosity of the medium and d the diameter of the particle, as is shown by the calculation of N, the Avogadro Number from the rate of fall of sol particles under gravity.[68] In the case of the diffusion of a large dissolved molecule, however, Glasstone, Laidler & Eyring[69] (p.521) show that the expression

$$D = \frac{kT}{0.5a\pi d\eta}$$

is /

is preferable where "a" does not differ appreciably from unity. Finally, in the case of a small dissolved molecule of the same type as the solvent molecule they show (p.519) that a more correct expression is

$$D = \frac{kT}{\alpha\eta}$$

as applied, for example, to the diffusion of heavy into light water.[70]

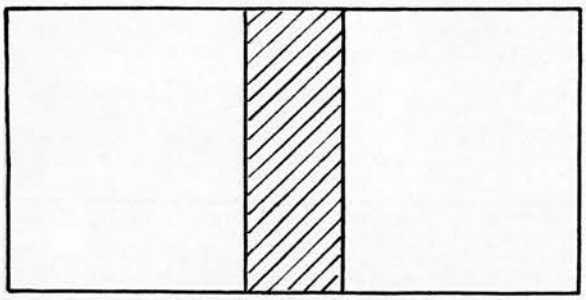
In the present case with a solute molecule of mass M_1, diameter α_1, in concentration x_1 and of volume V_1 we may include temporarily any such additional factor in the value of α and put

$$D \propto \frac{1}{\alpha\eta}$$

Since, in the case of the aqueous solutions used in the present investigation, the variation of T is in general small compared with variation in η, the temperature is at present omitted from this expression. The effect of the inclusion of T will be considered later.

In the case of gases the essential features of thermal diffusion were derived by considering the difference in diffusional characteristics in the hot and cold regions as determined by the relative concentrations of the gas molecules as given by the temperature. On analogous lines we would expect a general decreased concentration in the liquid state in the hot region, although the coefficient of expansion of liquids is in general /

general much less than the corresponding figure in gases. However the viscosity of the solution is in itself a measure of this effect.



The number of M_1 molecules passing in the first instance by thermal diffusion from region T to region $T+\Delta T$ is thus proportional to Δx_1 where

$$\Delta x_1 = \frac{x_1}{d_1} \cdot \frac{1}{\eta_{T+\Delta T}}$$

This flow must be balanced by a corresponding flow of M_1 and M_2 molecules in the reverse direction. Now in the gas theory the volumes of the different gas molecules were tacitly assumed to be the same, by Avogadro theory, for the same conditions; but in a liquid, in a more closely packed condition, this is not the case; distinction must be made between the volumes of the molecules, viz:- V_1 and V_2. The balancing flow is thus essentially a volume phenomenon.

Since /

Since the number of M_1 molecules above transferred from T to $T+\Delta T$ was Δx_1, their volume will be $\Delta x_1 V_1$ and this is the volume to be considered as counterbalancing the flow. The volume proportion of M_1 molecules in the returned volume will be $\Delta x_1 V_1 . \frac{V_1 x_1}{V_1 x_1 + V_2 x_2}$

and the number of M_1 molecules will be $\Delta x_1 V_1 . \frac{x_1}{V_1 x_1 + V_2 x_2}$

Thus collecting the various terms,

The number of M_1 molecules passing in the first instance

(a) from $T \rightarrow T+\Delta T$, $\quad \Delta x_1 = \frac{x_1}{\alpha_1} . \frac{1}{\eta_{T+\Delta T}}$

(b) from $T \rightarrow T-\Delta T$, $\quad \Delta x_1' = \frac{x_1}{\alpha_1} . \frac{1}{\eta_{T-\Delta T}}$

Similar expressions will hold for the M_2 molecules.

Considering now the return flow, the number of M_1 molecules

(a) moving $T+\Delta T \rightarrow T$ (i) due to Δx_1 moving $T \rightarrow T+\Delta T$

$$= \Delta x_1 V_1 \frac{x_1}{V_1 x_1 + V_2 x_2}$$

(ii) due to Δx_2 moving $T \rightarrow T+\Delta T$

$$= \Delta x_2 V_2 \frac{x_1}{V_1 x_1 + V_2 x_2}$$

(b) /

(b) moving $T-\Delta T \rightarrow T$ (i) due to $\Delta x_1'$ moving $T \rightarrow T-\Delta T$

$$= \Delta x_1' V_1 \frac{x_1}{V_1 x_1 + V_2 x_2}$$

(ii) due to $\Delta x_2'$ moving $T \rightarrow T-\Delta T$

$$= \Delta x_2' V_2 \frac{x_1}{V_1 x_1 + V_2 x_2}$$

and similarly for the M_2 molecules.

Thus excess of M_1 over M_2 molecules moving from $T-\Delta T \rightarrow T \rightarrow T+\Delta T$ is

$$\Delta S = \frac{V_1 + V_2}{V_1 x_1 + V_2 x_2}\left[x_2\left(\Delta x_1 - \Delta x_1'\right) - x_1\left(\Delta x_2 - \Delta x_2'\right)\right]$$

Substituting the values for Δx_1, Δx_2, etc.,

$$\Delta S = \frac{V_1 + V_2}{V_1 x_1 + V_2 x_2} \cdot \frac{x_1 x_2}{1}\left(\frac{1}{\eta_{T+\Delta T}} - \frac{1}{\eta_{T-\Delta T}}\right)\left(\frac{1}{d_1} - \frac{1}{d_2}\right)$$

In this general expression the viscosity factor is always positive since the viscosity of a liquid always decreases with temperature in contrast with gases. The direction of concentration change will therefore be determined by the diameter factor $\left(\frac{1}{d_1} - \frac{1}{d_2}\right)$: if this is positive the solute M_1 of diameter d_1 will migrate to the hot side corresponding to a smaller diameter d_1. For $d_1 > d_2$ the factor will be negative and the solute will concentrate in the cold region.

For /

For the integration of this expression over a finite temperature range, we must now include in the expression for D the temperature term

i.e., $$D \propto \frac{T}{d\eta}$$

The theory so far has been built on the assumption that the change in η as a result of change in temperature is large compared with the change in T, an assumption justified for the aqueous solution conditions only when one mean temperature is considered and the gradient applied at this temperature is not too large. For large gradients and variations of mean temperature, however, it is necessary to consider the introduction of the T factor.

In the theory of thermal diffusion above, separation is envisaged as a result of the carrying of temperature characteristics into a region where the diffusional characteristics are different, i.e., the molecule at temperature T is regarded as passing through a region of viscosity $\eta_{T+\Delta T}$: and the difference in path length from that of a molecule at temperature T passing through a region of viscosity $\eta_{T-\Delta T}$ is regarded as producing the separation. Accordingly, in the theory, all the factors, Δx, etc., are to be multiplied by T giving

$$\Delta S = f(x, M, V)\, T\left(\frac{1}{\eta_{T+\Delta T}} - \frac{1}{\eta_{T-\Delta T}}\right)$$

The /

The finite separation achieved will then be given by the integration of this expression. For this purpose we put $\frac{1}{\eta_{T+\Delta T}} - \frac{1}{\eta_{T-\Delta T}} = \Delta\left(\frac{1}{\eta}\right)$. We then have for a given solution in relation to T variation

$$\alpha S = KT\,\alpha\left(\frac{1}{\eta}\right)$$

Now $\eta = Ae^{\frac{B}{T}}$ to a close approximation[69], p 484, and therefore

$$\frac{1}{\eta} = \frac{1}{A}\cdot e^{\frac{-B}{T}}$$

Hence

$$\frac{\alpha\left(\frac{1}{\eta}\right)}{\alpha T} = \frac{1}{A}\cdot e^{\frac{-B}{T}}\cdot\frac{B}{T^2} = \frac{B}{A}\cdot e^{\frac{-B}{T}}\cdot T^{-2}$$

$$\therefore \quad \alpha S = KT\,\frac{B}{A}\cdot e^{\frac{-B}{T}}\cdot T^{-2}\alpha T = \frac{KB}{A}\cdot e^{\frac{-B}{T}}\cdot T^{-1}\alpha T$$

$$\text{and} \quad S = \frac{KB}{A}\int e^{\frac{-B}{T}}T^{-1}\alpha T$$

The integration of this expression gives

$$S = \frac{-KB}{A}\cdot\frac{e^{\frac{-B}{T}}}{-B}\cdot\frac{T}{1}\left[1 - \frac{T}{B} + 2!\left(\frac{T}{B}\right)^2 - 3!\left(\frac{T}{B}\right)^3 \cdots\cdots\right]$$

Now the variation of viscosity with temperature is given for such a solution to a close approximation by $\eta = e^{\frac{B'}{RT}}$ where $\frac{B'}{R} \fallingdotseq 2000 = B$ for the temperature range possible $(273 - 373^{0}A)$ $\therefore \frac{T}{B} \fallingdotseq \frac{300}{2000} \fallingdotseq \frac{1}{7}$.

The above series is therefore convergent and no great /

great error is introduced by taking $S = \frac{K}{A} \cdot \frac{T}{e^{\theta/T}} +$ constant.

The separation is thus $S_{T_1}^{T_2} = \frac{K}{A}\left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}\right) f(x, M, V)$

If throughout this derivation, the variation of temperature had been neglected, we should have obtained

$$S_{T_1}^{T_2} = \frac{K'}{A}\left(\frac{1}{\eta_2} - \frac{1}{\eta_1}\right) f(x, M, V)$$

This simpler expression was in fact used for some considerable time, since it was thought that temperature would have a relatively small effect. This is indeed the case - the relative values of the two expressions differ little from each other, and a numerical example illustrating this point will be given later. However, the complete expression including T has been used throughout the main part of the text..

This expression now gives what is really the initial rate of the Soret separation. What is actually observed, however, is the convected separation. The following assumption is now made:-

(The rate of convected thermal diffusion) =
(the rate of simple thermal diffusion) ×
(the rate of convection.)

An expression is therefore required for the rate of convection.

In his treatment of the same problem for the parallel /

parallel sided cell arrangement already described, P. Debye[55] gives for the rate of the convection current at the point a distance "x" from the cold wall

$$v = \frac{\beta g \rho T}{6\eta} a^2 \left(\frac{x}{a} - \frac{1}{2}\right)\left[\frac{1}{4} - \left(\frac{x}{a} - \frac{1}{2}\right)^2\right]$$

the hot wall being at a distance "a" from the cold wall and β = coefficient of cubical expansion, ρ = density, η = viscosity and T = temperature difference as before. This equation is derived on the assumption that the velocity will be zero at $x = 0$, $\frac{a}{2}$ and a. Presumably the velocity will be the same in magnitude but opposite in sign for all points symmetrically arranged about $x = \frac{a}{2}$ since each layer of liquid must make a complete circuit, because liquid cannot accumulate at any point. The viscosity at such points, however, must be different for the temperature will be different. We take the appropriate viscosity to be inserted in the above expression as the viscosity at the mean temperature of the column and assume that the factor containing x is constant.

Finally, assuming that this expression may be directly applied to the column we obtain

$$S \propto \frac{\rho \Delta T}{\eta_T} \cdot \frac{(V_1 + V_2)x_1 x_2}{V_1 x_1 + V_2 x_2} \cdot \left(\frac{1}{\alpha_2} - \frac{1}{\alpha_1}\right)\left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}\right)$$

where ΔT replaces T and η_T is the viscosity at the mean temperature, the viscosities at T_1 and T_2 being η_1 and η_2 respectively. "β" has been assumed constant for /

for the present: it will be discussed later. Throughout the present work "g" is constant and so it has been included in the proportionality constant. Nevertheless it should be noted that the rate of separation might be increased by increasing "g" by centrifugal methods such as those used by Farber and Libby[45] for gases, as has been suggested.[71]

In the expression α_1 and α_2 have been interchanged so that now if positive it represents the increase of M_1 over M_2 in the cold region (i.e., at the foot of the column - as measured experimentally). In using the expression it is to be noted that S is the separation achieved between x_1 and x_2. Thus if x_1 and x_2 are the initial concentrations in g-mols./litre and x_1' and x_2' are the final concentrations after the period of thermal diffusion

$$\begin{aligned} S &\equiv (x_1' - x_2') - (x_1 - x_2) \\ &\equiv (x_1' - x_1) - (x_2' - x_2) \\ &\equiv \Delta x_1 - \Delta x_2 \end{aligned}$$

where Δx_1 is the change in concentration of the solute as measured experimentally. Δx_2 may be obtained from Δx_1 by means of the relation :-

$$M_1x_1 + M_2x_2 = M_1x_1' + M_2x_2' = \text{mass of solution.}$$

i.e., $\Delta x_2 = (x_2' - x_2) = -\frac{M_1}{M_2}\Delta x_1$ which is inserted above to give

$$S = \Delta x_1 + \frac{M_1}{M_2}\Delta x_1$$

and finally $$S = \frac{M_2 + M_1}{M_2}\Delta x_1$$

where /

where M_2 is the molecular weight of water and M_1 that of the solute under consideration.

To facilitate comparison with the theory it has been usual in the present experiments to convert the measured Δx_1 into S making use of this relation.

Variation of Temperature Gradient.

(a) Experimental.

A solution of 30 g. glucose in 100 mls. solution was used throughout this series of experiments. Consequently for this series ρ, M and x_1 are constant and

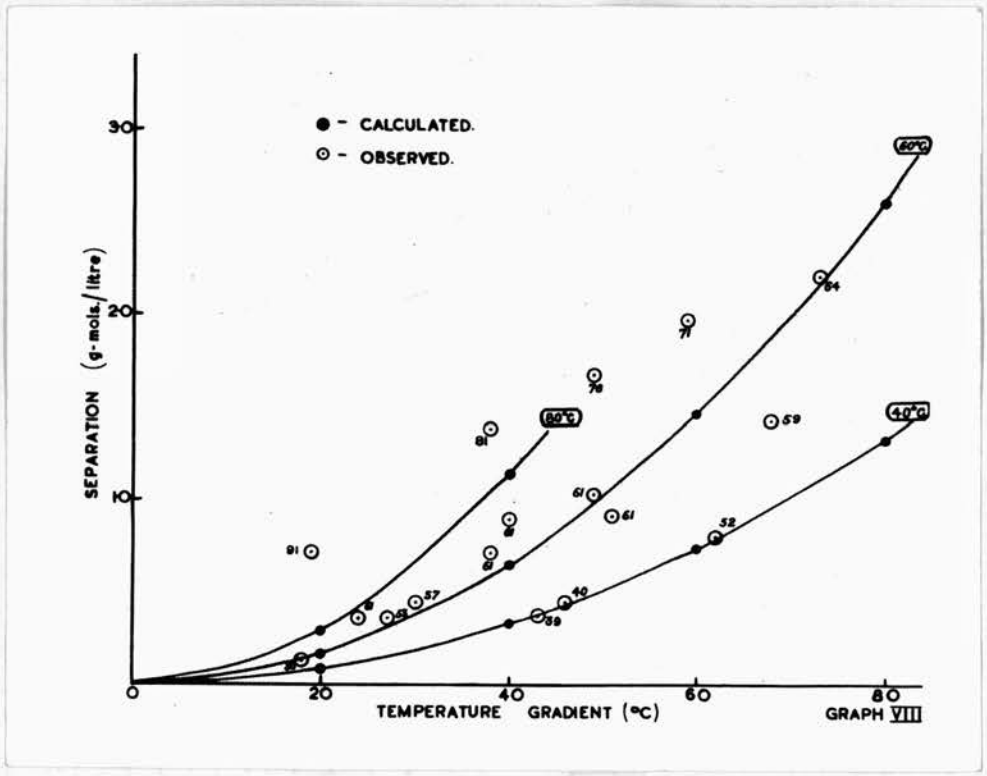
$$S = K' \frac{\Delta T}{\eta_{\bar{T}}} \cdot \left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1} \right)$$

where the gradient is defined by $\Delta T = T_2 - T_1$ and η_1, η_2 and $\eta_{\bar{T}}$ are viscosities at T_1, T_2 and $\bar{T}$ where $\bar{T} = \frac{1}{2}(T_1 + T_2)$ is the mean temperature of the column.

The glucose solution was introduced into the column and allowed to diffuse under the chosen gradient for 30 mins. A sample of the solution was analysed at this time and the change in molar concentration was taken as the initial rate for present purposes.

In the table of results given below (see also Graph VIII) the column $\bar{T}_{CORR.}$ refers to the application of a proportional correction to the observed mean temperature $\bar{T}$, as described in the experimental section. A correction is then required for the gradient in /

in cases where a correction is applied to the mean temperature and the corrected values are given in the column $\Delta T_{CORR.}$



GRAPH VIII

No. /

№	T_2	T_1	$\overline{T}$	$\overline{T}_{CORR.}$	ΔT	$\Delta T_{CORR.}$	Δx_1	$S^{OBS.}$
1	59	41	50	-	18	-	.0110	.127
2	66	39	53	-	27	-	.0325	.356
3	83	21	52	-	62	-	.0725	.795
4	72	42	57	-	30	-	.0400	.440
5	69	17	43	40	52	46	.0400	.440
6	60	16	38	-	44	-	.0365	.401
7	100	56	78	81	44	38	.1255	1.378
8	100	77	89	91	23	19	.0650	.712
9	100	32	66	71	68	59	.1790	1.968
10	100	43	72	76	57	49	.1520	1.670
11	100	16	60	64	84	73	.2005	2.204
12	80	42	61	-	38	-	.0650	.712
13	86	35	61	-	51	-	.0830	.910
14	81	41	61	-	40	-	.0815	.894
15	85	36	61	-	49	-	.0935	1.026
16	93	25	59	-	68	-	.1295	1.423
17	60	42	51	-	18	-	.0110	.127
18	73	49	61	-	24	-	.0325	.356
19	63	38	51	-	25	-	.0290	.320
20	62	17	39	-	43	-	.0340	.372

The S^{obs}-values are then plotted against the gradient in graph (VIII) and as a subscript to each point is attached the mean temperature to which it refers. The points lie on isothermals defined by the mean temperature, and it was decided to present these results by calculating some of the isothermals by means of the theoretical equation.

(b) Theoretical.

Of the constants required for this, and other similar calculations, which follow, many are viscosities. All viscosities are in millipoises. The main sources of this data are (1) International Critical Tables, (2) Landolt Bornstein Physikalische Chemische Tabellen, (3) Thorpe's Dictionary of Applied Chemistry (Glycerol). The values used were obtained by suitable interpolation and extrapolation as required - usually by graphical methods. The calculation of the isothermals now follows.

Glucose solution 30 g./100 mls. $S = K' \frac{\Delta T}{\eta_T} \left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1} \right)$

where $K' = 6.07 \times 10^{-3}$.

1. /

1. Mean Temperature 40°C.

ΔT	η/T	$\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}$	$\frac{\Delta T}{\eta/T}\left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_2}\right)$	$S^{CALC.}$
20	15.55	10.43	13.40	0.0814
40	"	20.89	53.75	0.3261
60	"	31.46	121.2	0.7360
80	"	42.27	217.5	1.321

2. Mean Temperature 60°C.

ΔT	η/T	$\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}$	$\frac{\Delta T}{\eta/T}\left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}\right)$	$S^{CALC.}$
20	10.38	13.74	26.49	0.161
40	"	27.43	105.7	0.643
60	"	41.54	240.2	1.460
80	"	55.55	428.5	2.600

3. Mean Temperature 80°C.

ΔT	η/T	$\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}$	$\frac{\Delta T}{\eta/T}\left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}\right)$	$S^{CALC.}$
20	7.425	17.39	46.82	0.284
40	"	34.66	186.9	1.135

The values of $S^{CALC.}$ are now inserted into graph (VIII) and lines drawn through them. It will be seen that in general the points lie close to the isothermals to which they refer. It is to be noted that the same constant /

constant has been used to calculate all three curves.

Variation of Mean Temperature.

(a) Experimental.

In the experiments which follow the temperature gradient was kept approximately constant and the mean temperature of the column varied. The general experimental procedure was the same as in the experiments just described. The gradient chosen was 40°C. and in this case not only was a solution of glucose (30 g/100 ml.) used but also one of sucrose (30 g./100 ml.) and one of glycerol (30 g./100 ml.)

Glucose Solution

No.	T_2	T_1	$\overline{T}$	$\overline{T}_{CORR.}$	ΔT	$\Delta T_{CORR.}$	Δx_1	$S^{OBS.}$
1	84	45	65	-	39	-	.089	.97
2	85	44	65	-	41	-	.096	1.05
3	61	21	41	-	40	-	.050	.55
4	60	21	41	-	39	-	.053	.59
5	46	5	26	25	41	39	.021	.234
6	46	5	26	25	41	39	.014	.157
7	100	60	80	83	40	34	.165	1.81
8	100	59	80	83	41	35	.172	1.89

Sucrose /

Sucrose Solution

No.	T_2	T_1	$\overline{T}$	$\overline{T}_{CORR.}$	ΔT	$\Delta T_{CORR.}$	Δx_1	$S^{OBS.}$
1	46	6	26	25	40	38	.0037	.074
2	100	59	80	83	41	35	.0849	1.80
3	100	58	79	82	42	36	.0778	1.56
4	63	21	42	-	42	-	.0332	.66
5	85	45	65	-	40	-	.0529	1.06

Glycerol Solution

No.	T_2	T_1	$\overline{T}$	$\overline{T}_{CORR.}$	ΔT	$\Delta T_{CORR.}$	Δx_1	$S^{OBS.}$
1	45	5	25	24	40	38	.0400	.245
2	100	60	80	83	40	34	.154	.942
3	60	19	40	-	41	-	.0565	.396
4	100	63	82	85	37	32	.1620	.991
5	78	38	58	-	40	-	.0730	.447
6	79	49	69	-	40	-	.1135	.694

These separations are now plotted against the mean temperature in Graph IX.

(b) Theoretical.

These separations have now been calculated taking $\Delta T = 40^{\circ}C.$ for mean temperatures of 20, 40, 60 and 80° C. Then taking suitable values for the constants, the resulting theoretical curves have been plotted on Graph IX /

IX using

$$S = \frac{K''}{\eta_T}\left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}\right)$$

Glucose.

T	η_T	$\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}$	$\frac{1}{\eta_T}\left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}\right)$	$S^{CALC.}$ $(K'' = 0.353)$
20	26.12	14.84	0.568	0.200
40	15.55	20.89	1.342	0.473
60	10.38	27.43	2.648	0.933
80	7.43	34.66	4.665	1.644

Sucrose.

T	η_T	$\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}$	$\frac{1}{\eta_T}\left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}\right)$	$S^{CALC.}$ $(K'' = 0.346)$
20	26.61	14.65	0.550	0.190
40	16.06	19.72	1.227	0.424
60	10.84	25.90	2.390	0.825
80	7.78	32.83	4.220	1.465

Glycerol.

T	η_T	$\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}$	$\frac{1}{\eta_T}\left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}\right)$	$S^{CALC.}$ $(K'' = 0.154)$
20	24.70	15.82	0.640	0.100
40	14.58	22.75	1.560	0.244
60	9.63	30.87	3.205	0.500
80	6.75	40.94	6.150	0.963

It will be observed that reasonably good agreement between /

between the calculated curves and observed points is found. The slight discrepancies are regarded as due to variation in the gradient. It will be seen that all the gradients as observed were very close to 40°C. The effect of the application of the correction was not realised until after the experiments had been completed.

Variation of Concentration: Various solutes.

Since it has now been shown that the equation represents the temperature dependence of the separation fairly closely, the dependence on concentration is now examined.

(1) Experimental.

For all these experiments, steam (100°C.) and cold water (10°C.) were used. Applying the usual corrections the actual gradient is then 80°C. and the mean temperature 60°C.

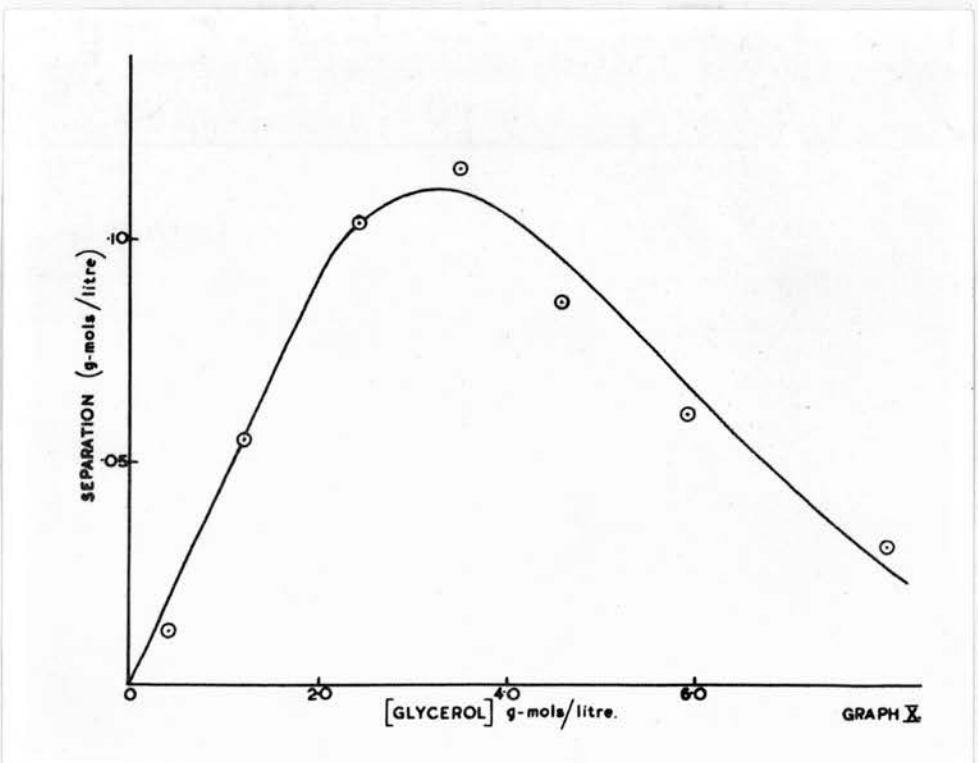
In all these experiments the initial rate was obtained graphically as described in the experimental section. The results were immediately converted into S values and graphed. A smooth curve was then drawn through the points and from it were read off at specified concentrations the values to be used for comparison with the theoretical values. For the present, only glucose, sucrose and glycerol are considered. The data for other solutes will be considered later.

Results /

Results.

(a) Glycerol.

Concentration (wt. %)	Specific Gravity	Concn. "X" (g-mol/litre)	Change in concn. per minute Δx_1	Separation S
3.75	1.009	0.411	0.002	0.012
10.80	1.026	1.205	0.009	0.055
21.10	1.052	2.410	0.017	0.104
29.60	1.074	3.449	0.019	0.116
38.50	1.098	4.592	0.014	0.086
48.50	1.125	5.930	0.010	0.061
64.20	1.169	8.035	0.005	0.031



Values from Graph X.

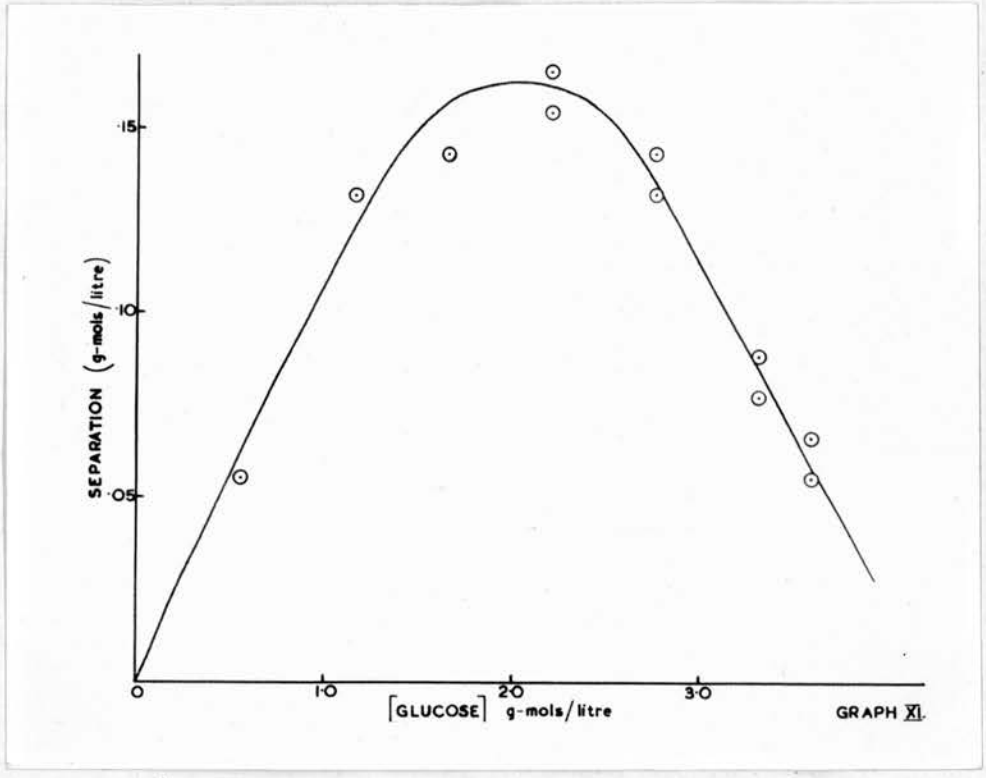
No.	x_1	$S^{obs.}$
1	1.158	0.059
2	2.410	0.104
3	3.449	0.111
4	4.592	0.102
5	5.930	0.072
6	8.035	0.029

(b) Glucose.

Concentration (g/100 mls)	Specific Gravity	Concn. "X" (g-mol/litre)	Change in concn. per minute Δx_1		Separation S	
10.00	1.037	0.555	0.005		0.055	
21.00	1.077	1.165	0.012		0.132	
30.00	1.109	1.665	0.013	0.013	0.143	0.143
40.00	1.148	2.220	0.014	0.015	0.154	0.165
50.00	1.185	2.775	0.012	0.013	0.132	0.143
60.00	1.220	3.330	0.007	0.008	0.077	0.088
65.00	1.237	3.605	0.005	0.006	0.055	0.066

Values from Graph XI.

No.	x_1	$S^{obs.}$
1	0.555	0.051
2	1.110	0.116
3	1.665	0.155
4	2.220	0.159
5	2.775	0.135

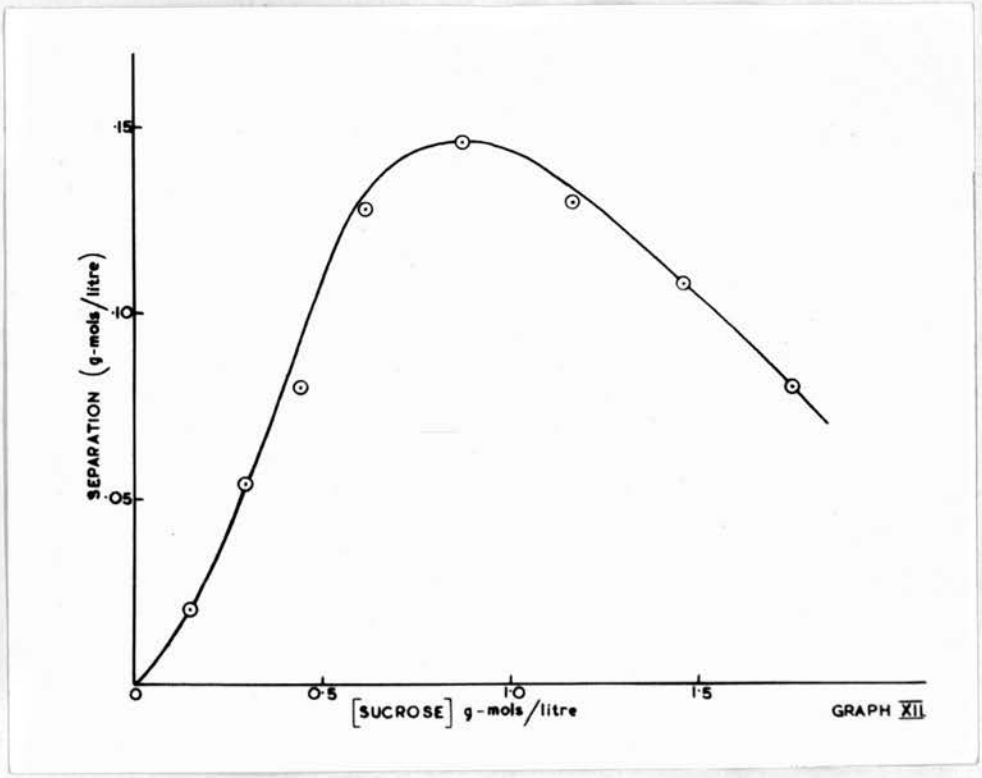


GRAPH XI.

(c) Sucrose.

Concentration (g/100 mls)	Specific Gravity	Concn. "X" (g-mol/litre)	Change in concn. per minute Δx,	Separation S
5	1.019	0.146	0.0010	0.020
10	1.037	0.292	0.0027	0.054
15	1.056	0.438	0.0040	0.080
21	1.077	0.614	0.0064	0.128
30	1.109	0.876	0.0073	0.146
40	1.146	1.168	0.0065	0.130
50	1.181	1.461	0.0054	0.108
60	1.218	1.753	0.0040	0.080

Values /



Values from Graph XII.

No.	x_1	$S^{obs.}$
1	0.292	0.054
2	0.614	0.128
3	0.876	0.146
4	1.168	0.130
5	1.461	0.108

(2) /

(2) Theory.

Since the gradient is constant throughout this series the appropriate expression for S is

$$S \propto \frac{\rho}{\eta_{\bar{T}}} \cdot \frac{(V_1+V_2)x_1x_2}{V_1x_1 + V_2x_2}\left(\frac{1}{d_2} - \frac{1}{d_1}\right)\left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}\right)$$

In the present series of experiments η_1, η_2 and $\eta_{\bar{T}}$ are the viscosities of the solutions in use at T_1 (100°C.) and T_2 (20°C.) and $\bar{T}$ (60°C.) respectively. ρ is the density at 20°C. The β factor which records the variation of density with temperature is discussed later.

The evaluation of V and d present some difficulty. In the first instance it is assumed that if the density σ of the substance is known, its molecular volume V is given by $\frac{M}{\sigma}$ where M is the "ordinary formula" molecular weight. For glycerol and for water the density in the liquid state is known, but no figures were found for the density of glucose or sucrose in the liquid state at room temperature. The densities of solid glucose and sucrose are available but are of little use on account of the doubtful volume change on melting.

The following procedure was adopted.

(i) it was assumed that the molecular volume of water was given by the molecular weight divided by the density at 20°C.

(ii) /

(ii) densities at 20°C. of solutions of all the solutes used containing 10 g. in 100 mls. were obtained, and by means of the identity

$$V_1x_1 + V_2x_2 = \text{volume of solution}$$

the apparent molar volume of the solute in dilute aqueous solution was calculated. It is realised that if the same calculation is carried out using the density of a more concentrated solution, the result obtained for V_2 will in general be slightly different. The percentage error is, however, small and it was therefore assumed that V was independent of concentration.

It is to be noted that some assumption is essential to obtain values of V_1 and V_2 separately, as distinct from $(V_1x_1 + V_2x_2)$.

For present purposes it was assumed that relative values of the diameter d were given by $V^{\frac{1}{3}}$ (This term comes up for discussion later.)

Data.

Substance	Sp.Gr. @ 18°C. of solid	Sp.Gr. @ 20°C. of liquid	Sp.Gr. @ 20°C. of aq. soln. (10 g/100 mls)
Sucrose	1.5877	-	1.03814
Glucose	1.5620	-	1.03769
Glycerol	-	1.2617	1.02210
Acetone	-	0.79046	0.998550
Water	-	0.99823	-

Using /

Using the figures in the last column the α and V terms may be evaluated.

Substance	Density σ from Sp.Gr. of solution	Molecular Weight M	g.mol. Volume V (mls.)	α $(\propto V^{\frac{1}{3}})$	$\left(\frac{1}{\alpha_2}-\frac{1}{\alpha_1}\right)\left(\frac{V_1+V_2}{V_1x_1+V_2x_2}\right)$
Sucrose	1.6615	342.30	206.03	5.9062	0.04750
Glucose	1.6493	180.16	109.23	4.7802	0.02150
Glycerol	1.3113	92.095	70.230	4.1258	0.01227
Acetone	0.88548	58.079	65.590	4.0329	0.01113
Water	0.99823	18.016	18.048	2.6231	-

The other terms in the expression for S vary with the concentration. Each term will be taken in turn, and the solutes considered in order for this term.

Term in x_1x_2 and $\frac{\rho}{\eta_T}$

(a) Glycerol.

No.	[Glycerol] g-mol/litre x_1	Specific Gravity ρ	[Water] x_2 (g-mol/litre)	x_1x_2	$\eta_{60^\circ C.}$	$\frac{\rho}{\eta}_{60^\circ C.}$
1	1.158	1.025	50.95	59.00	5.795	0.1770
2	2.410	1.052	46.05	111.0	7.340	0.1434
3	3.449	1.074	42.00	144.7	9.635	0.1115
4	4.592	1.098	37.49	172.1	11.75	0.0935
5	5.930	1.125	32.12	190.6	17.02	0.0661
6	8.035	1.169	23.82	191.4	33.59	0.0370

Glucose /

(b) Glucose.

No.	[Glucose] x_1 g-mol/ litre	Specific Gravity ρ	[Water] x_2 (g-mol/ litre)	x_1x_2	$\eta_{60°C.}$	$\frac{\rho}{\eta}_{60°C.}$
1	0.555	1.037	52.00	28.90	5.810	0.1780
2	1.110	1.076	48.60	54.00	7.360	0.1460
3	1.665	1.109	44.90	74.80	10.36	0.1070
4	2.220	1.148	41.50	92.10	13.81	0.0830
5	2.775	1.185	38.00	105.5	19.86	0.0600

(c) Sucrose.

No.	[Sucrose] x_1 g-mol/ litre	Specific Gravity ρ	[Water] x_2 (g-mol/ litre)	x_1x_2	$\eta_{60°C.}$	$\frac{\rho}{\eta}_{60°C.}$
1	0.292	1.037	52.00	15.03	5.882	0.1780
2	0.614	1.077	48.15	29.55	7.880	0.1366
3	0.876	1.109	44.90	39.38	10.86	0.1020
4	1.168	1.146	41.42	48.40	15.66	0.0732
5	1.461	1.181	37.82	55.20	22.22	0.0532

Term in T and η_T

(a) Glycerol.

No.	η_{100}	η_{20}	$\frac{373}{\eta_{100}} - \frac{293}{\eta_{20}}$
1	3.35	13.3	89.3
2	4.04	18.5	76.7
3	4.90	24.7	64.29
4	5.97	35.3	54.14
5	8.21	55.3	40.15
6	16.96	147.0	20.00

(b) Glucose.

No.	η_{100}	η_{20}	$\frac{373}{\eta_{100}} - \frac{293}{\eta_{20}}$
1	3.43	13.3	95.8
2	4.30	18.2	71.6
3	5.43	25.9	57.4
4	7.59	38.6	41.57
5	10.66	61.7	30.20

(c) Sucrose.

No.	η_{100}	η_{20}	$\frac{373}{\eta_{100}} - \frac{293}{\eta_{20}}$
1	3.45	13.2	85.8
2	4.50	18.7	67.2
3	5.86	26.9	52.8
4	7.76	42.3	41.10
5	12.10	76.4	26.97

Collecting the various terms the calculations may now be completed. Let $S^{calc.} = \frac{\rho}{\eta_{60}} \cdot \frac{x_1 x_2 (V_1 + V_2)}{V_1 x_1 + V_2 x_2} \left(\frac{373}{\eta_{100}} - \frac{293}{\eta_{20}} \right) \left(\frac{1}{d_2} - \frac{1}{d_1} \right)$

Glycerol

No.	x_1	S^{calc}	$S^{calc'}$
1	1.158	11.44	2.87
2	2.410	14.98	3.79
3	3.449	12.74	3.24
4	4.592	10.69	2.75
5	5.930	6.210	1.61
6	8.035	1.738	.45

Glucose

No.	x_1	S^{calc}	$S^{calc'}$
1	0.555	10.60	2.46
2	1.110	12.13	3.01
3	1.665	9.876	2.50
4	2.220	6.832	1.74
5	2.775	4.109	1.05

Sucrose

No.	x_1	S^{calc}	$S^{calc'}$
1	0.292	10.90	2.71
2	0.614	12.89	3.24
3	0.876	10.07	2.55
4	1.168	6.701	1.77
5	1.461	3.766	0.97

Now, /

Now, if instead of using $\frac{373}{\eta_{100}} - \frac{293}{\eta_{20}}$ we had used the form $\frac{1}{\eta_{100}} - \frac{1}{\eta_{20}}$ we should have obtained the results given in the column $S^{CALC'}$. Although the absolute magnitudes are not the same, the relative values differ by little within a series, and each series still bears the same relationship to the others as it did before.

The β term was not included in this expression due to the absence of sufficient data. International Critical Tables give densities at 15, 20, 25 and 30°C. only of various glycerol solutions and from these, mean values of β may be calculated for the range 15 - 30°C. The values which are obtained are -

Glycerol Soln. No.	1	2	3	4	5	6
$\beta \times 10^4$	3.26	3.67	3.80	4.00	4.14	4.46

Since no data is available for glucose or sucrose on this question, β has not been included in $S^{CALC.}$ for any of the solutes.

These S^{CALC} are now compared with the experimental values for S already described $(S^{OBS.})$ by consideration of the ratio $\frac{S^{OBS}}{S^{CALC}}$.

Glycerol /

Glycerol				Glucose				Sucrose			
x_1	$S^{OBS.}$	$S^{CALC.}$	$\frac{S^{OBS.}}{S^{CALC.}}$	x_1	$S^{OBS.}$	$S^{CALC.}$	$\frac{S^{OBS}}{S^{CALC}}$	x_1	$S^{OBS.}$	$S^{CALC.}$	$\frac{S^{OBS.}}{S^{CALC.}}$
1.158	0.059	11.44	5.16	0.555	0.051	10.60	4.82	0.292	0.054	10.90	4.96
2.410	0.104	14.98	6.94	1.110	0.116	12.13	9.22	0.614	0.132	12.89	10.25
3.449	0.111	12.74	8.71	1.665	0.155	9.876	15.88	0.876	0.146	10.07	14.50
4.592	0.102	10.69	9.54	2.220	0.159	6.832	23.30	6.168	0.130	6.701	19.40
5.930	0.072	6.210	11.59	2.775	0.135	4.109	32.88	1.461	0.105	3.766	27.90
8.035	0.029	1.738	16.69								

In considering these results two things are to be noted.

(i) at low concentrations the ratio of calculated to observed separation is the same for all of the three solutes considered. Deviations arise at high concentrations, and the higher the concentration the worse do the deviations become.

(ii) a maximum is obtained in $S^{OBS.}$ and $S^{CALC.}$, the positions of the maxima being -

	Glycerol	Glucose	Sucrose
Concn. at max. of $S^{OBS.}$	3.5	2.2	0.9
" " " " $S^{CALC.}$	2.4	1.1	0.6

which are seen to be of the same order and in the same sequence.

If the β values are included in S^{CALC} for Glycerol it is seen that the agreement would be slightly improved but this alone could not account for the discrepancies at high concns. since the β values change by about 30% whereas the discrepancies are of the order of 300%.

Since it has been shown that quite drastic alterations of the "η_T" term have little effect on the result, the discrepancies must be due to the "d" term.

In the evaluation of $S^{CALC.}$ the "d" term has been taken as independent of concentration and given by $\sqrt[3]{\text{molecular volume}}$. In the development of the theory, however, it was pointed out that "d" included a factor depending on the relative sizes of the diffusing molecule and the molecules of the medium. As the character of the medium alters on alteration of x_1 and x_2, the factor for the diffusing molecules (solvent and solute) will progressively alter. This may be allowed for semi-empirically, as follows, to show the direction in which such a change in "d" might operate.

When /

When the diffusing molecule is very large compared with the molecules of the medium

$$D \propto \frac{1}{3\pi\eta d} \propto \frac{1}{9d} \cdot$$

When the molecules are all of the same size

$$D \propto \frac{1}{\eta d} \propto \frac{1}{d}$$

Following the same trend when the diffusing molecule is smaller than the molecules of the medium, presumably the rate of diffusion will be faster still.

Thus, as the concentration of the solute increases, the rate of diffusion of the solute molecule will relatively increase: so also will the rate for the solvent molecule. If these increases are approximately the same for a given concentration change, the $\left(\frac{1}{d_2} - \frac{1}{d_1}\right)$ factor will progressively increase, i.e., the direction of this correction is such as to tend to decrease the drift in the previous S^{OBS}/S^{CALC} "constants."

The effect which increased solute concentration has on the correcting factor for diameter will depend on how rapidly the Stokes formula is approached, from the point of view of the relative sizes of the molecules. There appears to be no evidence on this point. The following semi-empirical treatment is devised simply to reduce as far as possible the drift of $S^{CALC.}$ to zero.

Consider the following expression for a correcting factor /

factor F:-

$$F = \frac{1}{9} + \frac{8}{x_1 + 9x_2}\left[\frac{x_1}{9\left(\frac{d_p}{d_1}\right)^7} + \frac{x_2}{\left(\frac{d_p}{d_2}\right)^7}\right]$$

The seventh power of the radius which is implicit in this expression may have some theoretical significance, p.471[68]. Consider as an example the case of glycerol and water.

Glycerol diameter $d_1 = 4.13$: Water diameter $d_2 = 2.62$.

1. Water diffusing through pure water. $x_1 = 0$, $\frac{d_p}{d_2} = 1$

$\therefore F_2 = 1$, corresponding to $D \propto \frac{1}{d}$

2. Water diffusing through pure glycerol. $x_2 = 0$, $\left(\frac{d_p}{d_1}\right)^7 = 0.042$.

$\therefore F_2 = 2.462$ which is >1 as desired.

3. Glycerol diffusing through pure water. $x_1 = 0$, $\left(\frac{d_p}{d_2}\right)^7 = 23.82$.

$\therefore F_1 = 0.4842$ which is <1 as desired.

4. Glycerol diffusing through pure glycerol. $x_2 = 0$, $\frac{d_p}{d_1} = 1$.

$\therefore F_1 = 1$, corresponding to $D \propto \frac{1}{d}$ again.

In the above, for simplicity, we have taken the determining factor to be molar concentration; more correctly the molar volume will be the deciding factor: hence take

$$F = \frac{1}{9} + \frac{8}{V_1x_1 + 9V_2x_2}\left[\frac{V_1x_1}{9\left(\frac{d_p}{d_1}\right)^7} + \frac{V_2x_2}{\left(\frac{d_p}{d_2}\right)^7}\right]$$

This, of course, gives the same extreme values as before for x_1 or $x_2 = 0$.

The constant term $\left(\frac{1}{\alpha_2} - \frac{1}{\alpha_1}\right)$ of the previous calculation is now to be replaced by $\left(\frac{F_2}{\alpha_2} - \frac{F_1}{\alpha_1}\right)$. In this calculation the variation of V_1 with concentration has been allowed for, so that $V_1 x_1 + V_2 x_2 = 1000$ mls. throughout, by assuming that V_2 (water) does not vary. S^{CALC*} indicates the corrected value of $S^{CALC.}$

1. Glycerol $\alpha_1 = 4.13$ $\left(\frac{\alpha_1}{\alpha_2}\right)^\gamma = 23.82$

$\alpha_2 = 2.62$ $\left(\frac{\alpha_2}{\alpha_1}\right)^\gamma = 0.04199$

No.	V_1x_1	V_2x_2	$\frac{F_2}{\alpha_2} - \frac{F_1}{\alpha_1}$	$\frac{S^{OBS}}{S^{CALC*}}$
1	82	918	0.420	1.695
2	170	830	0.513	1.875
3	244	756	0.606	2.000
4	325	675	0.728	1.820
5	421	579	0.905	1.780
6	571	429	1.317	1.760

2. Glucose $\alpha_1 = 4.78$ $\left(\frac{\alpha_1}{\alpha_2}\right)^\gamma = 66.73$

$\alpha_2 = 2.62$ $\left(\frac{\alpha_2}{\alpha_1}\right)^\gamma = 0.01499$

No.	V_1x_1	V_2x_2	$\frac{F_2}{\alpha_2} - \frac{F_1}{\alpha_1}$	$\frac{S^{OBS}}{S^{CALC*}}$
1	63	937	0.546	1.57
2	124	876	0.744	2.18
3	191	809	0.953	2.90
4	252	748	1.150	3.51
5	315	685	1.464	3.89

3. /

3. Sucrose $\alpha_1 = 5.91$ $\left(\frac{\alpha_1}{\alpha_2}\right)^Y = 293.38$

$\alpha_2 = 2.62$ $\left(\frac{\alpha_2}{\alpha_1}\right)^Y = 0.003409$

No.	V_1x_1	V_2x_2	$\frac{F_2}{\alpha_2} - \frac{F_1}{\alpha_1}$	$\frac{S^{OBS}}{S^{CALC*}}$
1	63	937	1.10	0.956
2	133	867	2.03	1.07
3	191	809	2.90	1.06
4	254	746	4.03	1.03
5	319	681	5.26	1.13

It will be seen that as a result of this treatment the effect of concentration has been largely eliminated in the various series. The agreement is least good for Glucose, which is possibly due to slight errors in the viscosity figures in this case, as viscosities at 100°C. had to be extrapolated from 50°C. - the highest temperature at which viscosities were available.

However, the agreement between the various series at low concentrations is not so good as before, and it would appear that this may be due to the values assigned to "α" being themselves incorrect. This factor will be discussed in connection with the results for acetone, which follow, because in this case the $\left(\frac{1}{\alpha_2} - \frac{1}{\alpha_1}\right)$ term is negative, which means that the method of calculating "α" which has been used so far, is not an appropriate method in the case of acetone.

Variation /

Variation of Concentration - Acetone.

(a) Experimental.

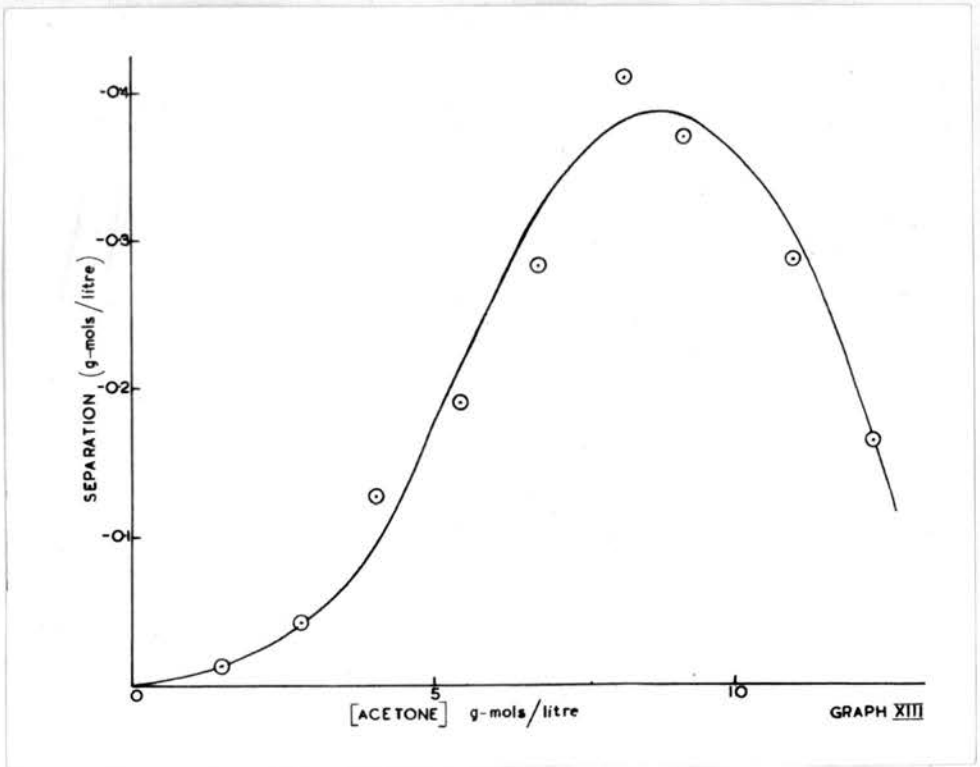
Since solutions of acetone commonly boil at temperatures well below 100°C., the use of steam as a method of heating was not possible. Water streams at 49°C. and 7°C. were used. Applying the usual corrections this corresponds to a gradient of 38°C. and a mean temperature of 26°C. (i.e., 45°C. to 7°C.) This was kept constant throughout the series.

For this series a sample of solution was withdrawn at 10 minutes after the start of diffusion and the change in concentration over this period divided by ten was taken as the initial rate. The method of analysis has been described in the experimental section and the initial rates are converted into S-values as usual. These values are then graphed - (Graph XIII) - and the values required for calculation read off.

Results /

Results.

[Acetone] ml/100 ml. ~~(g-mol/l)~~	[Acetone] x_1 (g-mol/l)	[Acetone] decrease per minute Δx_1	Separation S	Values from Graph	
				x_1	$S^{obs.}$
10	1.48	0.003	-0.013		
20	2.80	0.010	-0.042	2.741	-0.040
30	4.05	0.030	-0.127	5.481	-0.197
40	5.45	0.045	-0.190	8.228	-0.375
50	6.74	0.067	-0.283	10.960	-0.310
60	8.18	0.097	-0.410		
70	9.15	0.088	-0.372		
80	10.98	0.068	-0.287		
90	12.32	0.039	-0.165		



(b) Theoretical.

Despite the fact that it was known that the theory would predict for acetone a +ve separation, it was decided to apply exactly the same method of calculation to acetone solutions in order to see if the only anomaly was the changed sign.

The data required for this calculation is

[Acetone] mls./ 100 mls	Sp.Gr.	[Acetone] x_1 (g-mol/ litre	[Water] x_2 (g-mol/ litre)	η_{45}	η_{26}	η_{γ}	V_1x_1	V_2x_2
20	.9810	2.741	45.59	7.45	12.00	21.5	178	822
40	.9582	5.481	35.48	8.30	13.70	22.8	360	640
60	.9274	8.228	24.93	7.58	12.23	22.7	551	449
80	.8775	10.96	13.32	5.40	7.80	11.7	760	240

together with the data already given at the beginning of the section. The various terms in the calculation of S then are:-

[Acetone] mls/ 100ml	$\frac{\rho}{\eta_{26}}$	x_1x_2	$\frac{318}{\eta_{45}} - \frac{280}{\eta_{\gamma}}$	$\frac{F_2}{d_2} - \frac{F_1}{d_1}$	$\frac{V_1+V_2}{V_1x_1+V_2x_2}$	S^{CALC}*	S^{OBS}	$\frac{S^{OBS}}{S^{CALC}}$*
20	0.0817	125.0	29.2	0.4921	0.0834	12.3	-0.040	-.325
40	0.0699	194.5	26.0	0.7174	"	21.2	-0.197	-.929
60	0.0758	205.1	29.4	1.106	"	45.4	-0.375	-.822
80	0.1125	146.2	35.0	1.995	"	95.9	-0.310	-.323

It /

It is seen that there is no regularity to be observed in S^{OBS}/S^{CALC}*. It is well known that the coefficient of cubical expansion β of organic liquids, such as acetone, is much greater than that of water, so presumably β might vary quite appreciably with concentration. Such a correction might smooth the values out somewhat, but could not explain the negative sign. As already stated, this must be due to the method of evaluation of the "d" factor which accordingly cannot be correct for acetone.

The "d" factor.

So far "d" has been taken as $\propto \left(\frac{M}{\sigma}\right)^{\frac{1}{3}}$ where σ is the apparent density of the solute in solution and M is its molecular weight. This value of course refers to the volume which the molecule appears to occupy in the solution and includes the "free space" in which molecular movement or oscillation must be assumed to take place.

In the case of glycerol and the sugars the molecular "diameter" calculated in this way is greater than that similarly obtained for water, and the experimental direction of solute concentration is thus in agreement with the formula.

On the other hand the molecular diameter of acetone is approximately the same as glycerol on this basis, the decrease in molecular weight from 92 to 58 being counterbalanced by a decrease in density from 1.0 to 0.8.

If /

If this method of calculation sufficed, the direction and rate of the thermal diffusion of acetone would be approximately the same as for glycerol - in direct opposition to experiment. It may be noted here that any association of water molecules in the sense that the diffusing water "molecule" is a "doublet" or higher complex $(H_2O)_n$ with a correspondingly higher molecular weight would not remove this discrepancy. It is true that the extent to which glycerol may be expected to associate is greater than the corresponding association of acetone but further extension of such corrections to analogous examples of other alcohols leads to no uniform representation. In a similar way, for equal sizes of acetone and glycerol molecules, the factor of the diffusion coefficient which was included in "d" must be approximately constant for a given concentration: again there seems to be no explanation by this method whereby acetone may be distinguished from glycerol. In general it would appear that the calculation of relative diffusion diameters by the molecular volume method is not sufficiently accurate for the purpose.

A distinction between the "molar volume diameter" and the diffusion diameter has already been noted by Glasstone Laidler and Eyring[69] (p.521) for heavy water from the experimental results of Orr and Butler.[70] Calculation shows that the plane of flow in diffusion tends /

tends to coincide with the plane of the water molecule, since flow in this direction will take place most easily. In the same way the effective diffusion diameter of acetone must be much less than that calculated from the molar volume.

In general, however, comparison with thermal diffusion results obtained by other workers shows that acetone is not an isolated case in which the molecule of larger molar volume migrates to the hot region. Gillespie and Breck[50] have pointed out that, in general, that component, addition of which to the mixture causes the density to decrease, tends to accumulate at the top of the column. The results of Korsching and Wirtz[47c] may similarly be quoted.

Mixture	Component enriched at top of Column	Component of Lower Density
H_2O, D_2O	H_2O	H_2O
" , CH_3OH	CH_3OH	CH_3OH
" , C_2H_5OH	C_2H_5OH	C_2H_5OH
" , C_4H_9OH	C_4H_9OH	C_4H_9OH
C_6H_6, Thiophene	C_6H_6	C_6H_6
" Cyclohexane	nil	Cyclohexane
Cyclohexane, CCl_4	Cyclohexane	Cyclohexane
" n-hexane	n-hexane	n-hexane
" o-dichlorobenzene	Cyclohexane	Cyclohexane
Chlorobenzene, Toluol	Toluol	Toluol
n-Hexane, n-Octane	n-Hexane	n-Hexane
n-Hexane, CCl_4	n-Hexane	n-Hexane

The /

The present results are in agreement with this generalisation: but it is to be noted that exceptions may apparently occur. Thus in the above table no separation was found with benzene and cyclohexane although the difference in densities is not less than in the case of *n*-hexane and *n*-octane for which a separation was recorded. Berchem[3] also, in a Soret experiment, records the accumulation of ammonia of less density in the cooler region and was careful to ensure that the apparatus was so arranged that convection did not destroy the separation. It would appear, however, that if density is not the determining factor, it is a property closely allied to it.

It is first necessary to enquire whether the experimental method involving convection is not introducing a factor independent of the actual thermal diffusion across the elementary strip. In such convection, determined by gravity, the tendency will always be for the liquid of less density to accumulate at the top. There is therefore the possibility that the net movement of acetone, say, is to the cold region as with glycerol, but the resultant density is less than that of the original mixture and might cause the convection to "reverse."

It is to be noted that early experiments by Wereide[5] by the Soret method, involving no convection, gave a separation to the cold region of aqueous solutions /

solutions of glycerol, etc., but no observed separation of acetone or of methyl or ethyl alcohols, all of which are of density less than that of water. This then might be the result of two competing influences, thermal diffusion to the cold region, balanced by convection in the system.

Attempts were thus made to establish the direction of the separation by a Soret experiment with no convection in operation.

The apparatus used was the inverted V-tube described in the experimental section. This design was chosen in order to prevent convection obliterating separation: no matter to which side the acetone might diffuse, the arrangement should be hydrodynamically stable. The apparatus was filled with a solution of 50% by volume of acetone in water, and sealed. Water at 50°C. was passed rapidly round one side of the apparatus, and water at 5°C. round the other. The diffusion was allowed to proceed without interruption for 66 hours, because it was realised that the separation, if any, would be small. After this time samples were withdrawn and introduced into the cell of a Zeiss Interferometer. The separation observed was hardly measurable, but the direction of this change was such as appeared to indicate that some acetone had migrated to the hot region.

A return was therefore made to the convection column /

column with three methods of approach -

(a) the time of diffusion was cut down to a minimum consistent with measurement of concentration change: any change in density would thus be small and slight enough not to reverse the normal direction of convection.

Results: The Interferometer was used with a 10% by volume solution. Even after only 30 seconds diffusion some acetone had left the foot of the column.

(b) the concentration of the solution was reduced as far as possible: it is to be noted that the separation with acetone solution is surprisingly small at low concentrations, compared with, say, glycerol, or even compared with the separations it itself gives at higher concentrations. Korsching and Wirtz record the same kind of behaviour in alcohol/water mixtures, at low alcohol concentrations[47c] (p.264). It was thought possible that at very low concentrations the separation might be positive, corresponding to the case of neon-ammonia mixtures in gases.[42]

Results: 1% (vol.) solution. Interferometer used. 30 seconds detectable reduction in acetone concentration at the foot of the column.

(c) a ternary mixture of water, glycerol and acetone was examined: if acetone really migrates to the cold side, the simultaneous migration of glycerol would bring /

bring the density up to a value such that normal convection takes place.

Results: For details see experimental section.

	Sample B		Sample C	
	Original Concn. (g-mol/ litre)	Final Concn. (g-mol/ litre)	Original Concn. (g-mol/ litre)	Final Concn. (g-mol/ litre)
Acetone	0.09616	0.0935	0.1374	0.1262
Glycerol	0.2965	0.4050	0.1648	0.2950

Thus the glycerol goes to the cold side and the acetone to the hot side in both cases.

As a result of these experiments there seems to be no doubt that acetone really migrates to the hot region in the first instance and that the reason, in relation to the general equation, lies in over-simplification of the diffusion diameter. It is therefore necessary to enquire further into its theoretical derivation.

Eyring has based the derivation of the diffusion expression, on the general basis of liquid viscosity, on the assumption that viscosity being a flow or rate process, can be treated by the method of absolute reaction rates, as follows (cf. Chapter IX of ref. 69).

If two layers of molecules in a liquid at a distance λ_1 apart slide past each other under the influence /

influence of an applied force f dynes per sq. cm. displacing one layer with respect to the other: and if Δv is the difference in velocity between the two layers, the viscosity is by definition.

$$\eta = \frac{f\lambda_1}{\Delta v}$$

The motion of one layer with respect to the other is then taken to involve the passage of a molecule from one equilibrium position to another such position in the same layer; for this a suitable hole must be available, the production of such a hole requiring energy used in pushing back other molecules. With λ as the distance between two equilibrium positions in the direction of motion, λ_2 the distance between two neighbouring molecules in the same direction (λ may be equal to λ_2 but this is not necessarily so) and λ_3 the mean distance between two adjacent molecules in the moving layer in the direction at right angles to the direction of motion, the viscosity η may now be expressed by

$$\eta = \frac{\lambda_1}{\lambda_2\lambda_3\lambda^2} \cdot \frac{kT}{K} = \frac{\lambda_1 h}{\lambda_2\lambda_3\lambda^2} \cdot \frac{F}{F_{\neq}} e^{\frac{\varepsilon_0}{RT}}$$

where h is Planck's constant, k is the Boltzmann constant for a single molecule, ε_0 is the energy of activation at $0^\circ K$ i.e., the height of the energy barrier, and K thefrequency with which a molecule passes over the barrier. F and $F_{\neq}$ are partition functions /

functions of the molecule in the activated $(\neq)$ and initial states.

The process of diffusion is regarded as similar to that of viscous flow in that two successive equilibrium positions are involved at a distance apart of λ'. The diffusion coefficient is obtained as

$$D = (\lambda')^2 K'$$

This equation can only hold for ideal solutions or dilute solutions which approximate to ideal behavious. Two cases must then be considered -

(a) If λ' and K' for diffusion are identified with the corresponding quantities for viscosity, as is particularly the case for self diffusion, when the diffusing molecule is of the same type and size as the molecules of the medium the diffusion coefficient becomes

$$D = \frac{\lambda_1 kT}{\lambda_2 \lambda_3 \eta}$$

and if $\lambda_1 = \lambda_2 = \lambda_3 = \alpha$,

$$D \propto \frac{1}{\alpha \eta}$$

In the diffusion of heavy through light water previously mentioned λ_1 is found to be somewhat less than $(\lambda_2 \lambda_3)^{\frac{1}{2}}$, thus showing that the diffusional diameter α is not strictly appropriate even in the case of self-diffusion.

(b) When a large molecule diffuses through a solvent /

solvent of relatively small molecules, it is regarded as unlikely that the rate-determining step is the jump of the solute molecule from one equilibrium position to the next, because of the large energy which would be required. The temperature coefficient of diffusion is in fact the same as that of the solvent viscosity: it is much more probable that the jump of the solvent molecule is the rate-determining process, the solute molecule then moving into the vacant space. The diffusion coefficient obtained on this basis is then

$$D \propto \frac{1}{a\pi r\eta}$$ where "a" is a factor of the order of unity, which allows for the fact that the small solvent molecule may not take the shortest path in its journey round the large solute molecule; and r is the radius of the solute molecule. This is less than the previous value for self-diffusion by a factor of approximately 1.5.

Absolute values of diffusion rates have been calculated by evaluation of the appropriate partition functions: at constant temperature and in dilute solutions, in one solvent, relative values of D are inversely proportional to $m^{\frac{1}{2}}$ where "m" is the reduced mass of the solute and solvent molecules treated as a combined unit.

Some comparisons are given below for aqueous solution.

Solute /

Solute	Temperature(°A)	$D \times 10^5$ (cm² sec.⁻¹) Calculated	Observed
Methyl Alcohol	291	0.39	1.37
Amyl Alcohol	291	0.34	0.88
Glycerol	293	0.36	0.83
Glucose	291	0.32	0.57
Sucrose	293	0.34	0.57

The calculated values are of the correct order of magnitude, but for our present purpose do not appear sufficiently accurate to be used in calculation of the relative rates of diffusion. In such a treatment there appears to be no general correlation between density and rate of diffusion; indeed, in the previous calculation, the coefficient for water itself would be greater than all the others, and methyl alcohol would thus be expected in thermal diffusion to concentrate in the cold region in contrast to experiment.

The equations so far quoted have neglected any deviation from ideal behaviour. For non-ideal systems the diffusion coefficient becomes

$$D = D^{\circ} . \frac{d \log_e a_1}{d \log_e N_1}$$

where D° is the coefficient for the ideal system. Here the activity $a_1 = N_1 \gamma_1$ where γ_1 = activity coefficient of solute and N_1 = mole fraction of solute.

Now the activity of the component (1) is proportional to its partial vapour pressure p_1 in the mixture /

mixture, so we have

$$D \propto \frac{1}{d\eta} \cdot \frac{d \log_e p_1}{d \log_e N_1}$$

In comparing the group "glycerol and the sugars", which thermally diffuse to the cold region, with "acetone and the lower alcohols" which diffuse to the hot region, it is obvious from their respective volatilities and the vapour pressure of their solutions that we have here a corresponding grouping which does seem to be generally related to the diffusion process. The greater the increase in vapour pressure, per mole of solute added, the greater will be the diffusion coefficient and the less the tendency to diffuse thermally to the cold side. It would therefore appear that in discussing the thermal diffusion of such solutes, the appropriate activity coefficients must be included: since the activity coefficients will vary with the concentration it is possible that some examples may be found where diffusion will take place to the hot region at one concentration and to the cold region at another. Let us consider first the case of sucrose solutions for which activities have been determined[73]. At low concentrations the activity correction operates in such a way as to improve the agreement between calculated and observed separations. At high sucrose concentrations however the agreement is less good and eventually the "α" factor /

factor is caused to change sign, corresponding to diffusion of sucrose to the hot wall, which is in direct opposition to experiment. The conclusion is that the activity correction in itself is not a complete explanation of the difference between calculation and experiment in the case of non-volatile solutes. In the same way review of available data for acetone and the lower alcohols shows that an activity correction alone will not explain the uniformly negative sign observed with volatile solutes: thus we are led once more to the conclusion that the method of evaluation of the diffusion diameter is incorrect for solutes whose character differs appreciably from that of water itself. The experimental results may be taken to indicate that such molecules diffuse with their longer axis parallel to the direction of motion and so present a smaller "front" to the medium; this seems to be as far as we can take the matter, at present, from this point of view.

Discussing the matter now, more generally, the observation that acetone diffuses to the hot side while glycerol diffuses to the cold side, corresponds, on the basis of the present theory, to the fact that in its aqueous solutions acetone diffuses faster than water while glycerol diffuses more slowly than water, i.e., it is the rate of diffusion of the solute relative to that of water in the same solution which is the deciding factor. Consider then the case of water and glycerol /

glycerol molecules diffusing through a mixture of glycerol and water. Both glycerol and water molecules tend to form hydrogen bonds between themselves, and each other. The diffusion of the water molecule may thus be regarded as retarded by these bonds which have to be broken before diffusion can occur; much the same sort of considerations may be taken to apply to the glycerol molecule. As a result, the diffusional characteristics - other than volume - are similar and the rate of diffusion will be determined by the relative sizes of the molecules. In the case of a solution of acetone in water on the other hand, although a certain amount of enolisation may be visualised as taking place the molecule will suffer much less from hydrogen bond retardation than the water molecule, and as a result despite its greater bulk it will diffuse more rapidly than the water molecule and thus accumulate at the hot side. It does not seem surprising that the diffusion "constant" should change with concentration on this basis, because change in concentration corresponds to a change in environment. Direct evidence for the concentration dependence of the diffusion coefficient has been given by Fürth and co-workers,[74] using the micro-diffusion technique. They have shown that only in "very dilute liquid solution" does the diffusion coefficient remain constant. In the case of glycerol, at low /

low concentrations, the variation is, it happens, not very great but in some cases, e.g., urea, the variation is considerable, and for electrolytes greater still. Further experimental work of wider scope is clearly required, on the effect of concentration in the case of both thermal and simple diffusion.

Two Solutes. Let us now consider the possibility of separating two substances dissolved in water by thermal diffusion. The rate of separation of each solute will depend on the difference between its rate of diffusion and that of water in the solution. As a result, if each diffuses at a rate which is quite appreciably less than that of water - a condition which is commonly fulfilled since a large separation of each solute from solution is usually desired - the respective differences in rate in relation to water may differ little from each other, and the separation of one solute with respect to the other will be negligible in comparison with the total separation of them both from water. Further the relative rates of separation of the two solutes will more closely approach each other as the absolute magnitudes of the rates decrease. Thus, since the rate is controlled inter alia by the size of the diffusing particle, it appears that this method will be unsuitable for the separation of large molecules from each other, (e.g., starches, proteins or isotopes of uranium /

uranium, using solutions of uranium salts, as has been suggested[75]). On the other hand, there might seem good reason to suppose that the method would be useful for the removal of low molecular weight compounds from those of high molecular weight, e.g., salt from protein solutions which is at present carried out by the rather slow method of dialysis. However, there appears to be no record of successful separations in a case such as this.

All this, however, applies to the aqueous solution conditions of the present experiments. If a solvent were found in which one of the solutes diffused to the hot wall while the other went to the cold wall there seems to be every reason to suppose that separation would be rapid and efficient, just as in the case of acetone and glycerol in water already described. This method of attack would seem to offer the greatest possibilities.

However, in view of the fact that partial separations had been accomplished in cases where both solutes went to the foot of the column (for an aqueous solution of electrolytes[47b] and a benzene solution of steroids[47c]) it was decided to attempt a separation of two non-electrolytes from aqueous solution in a similar way.

Experiments /

Experiments with Two Solutes.

For these experiments two pairs of solutes were considered: (1) Glucose + Sucrose; (2) Glycerol + Sucrose: the results of these experiments now follow.

(1) Glucose + Sucrose.

The method of analysis is described in the experimental section where it is noted that in this case all that is required is the factor by which the concentration of each solute has changed at the time in question. If these factors be now divided the one by the other the resulting ratio will be a measure of the relative rates at which the two solutes have concentrated.

Expt. 1. Initial [Glucose] 1.00 g-mol/litre

Initial [Sucrose] 1.00 g-mol/litre

Time (min)	Factor for [Glucose] increase	Factor for [Sucrose] increase	$\frac{\text{[Sucrose] factor}}{\text{[Glucose] factor}}$
0	1.00	1.00	1.00
2	1.02	1.00	0.98
5	1.02	1.00	0.98
10	1.05	1.03	1.02
20	1.08	1.03	1.05
30	1.10	1.05	1.05
115	1.10	1.09	1.01

Expt. /

Expt. 2. Initial [Glucose] 2.00 g-mol/litre

Initial [Sucrose] 1.00 g-mol/litre

Time (min)	Factor for [Glucose] increase	Factor for [Sucrose] increase	[Sucrose] factor / [Glucose] factor
0	1.00	1.00	1.00
5	1.04	1.03	0.99
10	1.04	1.04	1.00
20	1.04	1.03	0.99
30	1.04	1.04	1.00
120	1.04	1.03	0.99

Expt. 3. Initial [Glucose] 0.50 g-mol/litre

Initial [Sucrose] 1.00 g-mol/litre

Time (min)	Factor for [Glucose] increase	Factor for [Sucrose] increase	[Sucrose] factor / [Glucose] factor
0	1.00	1.00	1.00
5	1.03	1.03	1.00
10	1.17	1.09	0.93
120	1.17	1.12	0.96

Expt. 4. Initial [Glucose] 2.00 g-mol/litre

Initial [Sucrose] 0.50 g-mol/litre

Time (min)	Factor for [Glucose] increase	Factor for [Sucrose] increase	[Sucrose] factor / [Glucose] factor
0	1.00	1.00	1.00
5	1.02	1.05	1.03
11	1.02	1.07	1.05
120	1.12	1.15	1.03

Expt. /

Expt. 5. Initial [Glucose] 3.00 g-mol/litre

Initial [Sucrose] 0.50 g-mol/litre

Time (min)	Factor for [Glucose] increase	Factor for [Sucrose] increase	$\frac{\text{[Sucrose] factor}}{\text{[Glucose] factor}}$
0	1.00	1.00	1.00
5	0.98	1.13	1.15
10	0.97	1.09	1.12
15	0.99	1.17	1.21
120	1.02	1.17	1.15

If now, for all the solutions used, the ratio $\frac{\text{[Sucrose] factor}}{\text{[Glucose] factor}}$ is averaged for time 10 mins. - corresponding to initial rate conditions - and also for 120 mins., which is perhaps closer to equilibrium conditions, we obtain

Time (mins)	$\frac{\text{[Sucrose] factor}}{\text{[Glucose] factor}}$
0	1.00
10	1.03
120	1.03

which shows that despite variations, due to difficulties on the experimental side, a small separation is observed, which is in the expected direction on the basis of the general theory. Examination of the individual results shows that if the sucrose concentration is less than or equal to that of the glucose, better separations are obtained in a short time than in a long time. But if the sucrose concentration exceeds that of the glucose /

glucose the separation appears to go the other way and the glucose is preferentially concentrated, contrary to expectation.

(2) Sucrose + Glycerol.

The separations obtained in the above experiments were much smaller than had been expected even having regard to the comparatively high molecular weights of both solvents; for even although this is so, the molecular weight of one is approximately twice that of the other. However, it was decided to make the ratio of the molecular weights of the solutes even higher by investigation of the system Glycerol-Sucrose-Water. In this case, in view of the fact that the above experiment with Glucose and Sucrose seemed to show:-
(a) that there was no advantage in having a disproportionately large amount of either component present.
(b) that no advantage was gained by extending the duration of the experiment,
— it was decided to carry out one experiment only.

In this experiment the solution used contained glycerol and glucose in equimolecular amounts. One analysis only was carried out 10 minutes after commencement of diffusion. It seemed best to carry out a large number of determinations on the same sample since the experimental technique was rather difficult.

Results /

Results (See Experimental Section)

Factor by which [sucrose] was increased	1.22
" " " [glycerol] " "	1.16

$$\frac{\text{[Sucrose] factor}}{\text{[Glycerol] factor}} = 1.05$$

Thus the separation is in the correct direction on the basis of the theory, and of the correct magnitude compared with the experiments on glucose and sucrose; it is, however, undeniably small.

The general conclusion, on these experiments with two solutes, is that no large separation is readily obtained under the conditions of the experiments.

The study of such separations is of great theoretical interest, for it enables comparisons to be made between the diffusion constants of two solutes under conditions such that the general environment is the same for both. In particular, the rate of convection, the viscosity and the temperature conditions, are all identical, which is clearly a unique advantage. However, it had become quite clear in the course of the experiments just described, that the difficulty of the analysis of mixtures such as these, made such an investigation a major problem and not one which could be satisfactorily attacked as a sideline to the present research: accordingly, no further experiments of this kind were carried out.

The Separation at Equilibrium

It will have been noted in the introduction that, in a description of some experimental work carried out by Ritchie and Taylor[49] on the convective thermal diffusion of copper sulphate solution, some solid crystallised out, after several hours diffusion. It has also been noted[26] that copper sulphate gives a large Soret effect, so it is interesting to note this further parallelism between the two effects. The point which is of present interest is to examine whether the equilibrium separation of sucrose passes through a maximum at 30 g./100 mls., where the maximum occurs in the initial rate curve, or at some higher concentration, or whether solid will be deposited in this case also.

A preliminary investigation was first carried out to see how long it was necessary to run the experiments in order to obtain values which would be proportional to the equilibrium separations. It was not intended to proceed to complete equilibrium as this is approached at an ever decreasing rate, and thus would require a very long time for each experiment. For these experiments a solution of 30 g. sucrose in 100 ml solution was used. A sucrose solution of this concentration gives the maximum initial rate value

Results /

Results.

Time (hrs)	[Sucrose] g-mol/litre	[Sucrose] increase g-mol/litre
0	0.876	-
5	0.965	0.089
15	0.970	0.094
30	0.972	0.096

In the light of these results it was decided that 5 hours would be sufficient for the purpose.

Accordingly solutions of sucrose of various concentrations were subjected to thermal diffusion in the column for five-hour periods, as follows:-

Initial [Sucrose] g-mol/litre (x_1)	[Sucrose] increase g-mol/litre Δx_1	Equilibrium Separation $S^{EQUIL.}$ (average)	Initial Rate $S^{OBS.}$
0.876	0.106; 0.089	1.96	0.146
1.168	0.141; 0.135	2.76	0.130
1.461	0.173; 0.183	3.56	0.108
1.753	0.207	4.14	0.080

The experimental values in column (2) were averaged and converted into S values $\left(S = \frac{M_2 + M_1}{M_2} \Delta x_1\right)$ as usual. The values for the initial rate are included for comparison. The $S^{EQUIL.}$ values are plotted against concentration in Graph XIV. It is seen that the curve does not turn over below 1.753 M (60 g/100 ml), although /

although it appears to fall off slightly at high concentrations. This last solution was exceedingly viscous and the column took quite a long time to fill with solution. More concentrated solutions were not investigated. In view of the tendency of sugar to form a syrup it seemed more likely that the solution would just get more and more syrupy rather than form solid. The separation will in due course become less for it must finally reach zero when the water concentration becomes zero.

There seemed to be some possibility that, in the course of an experiment of long duration, such as this, some inversion of the sucrose in solution might have occurred. In order to test this point some sucrose solution, in a stoppered conical flask, was placed in a boiling water bath and kept there for 5 hours. The refractometer reading of this solution at the end of this time was the same as at the beginning, thus showing that no change of this nature had occurred.

Variation of the Concentration: Xylose and Raffinose.

Brief mention should be made of four initial rate experiments which were carried out - two with xylose and two with raffinose. In both cases the solutions were made up by dissolving a known weight of the pure solute in a known volume of solution. The xylose was anhydrous ($C_5H_{10}O_5$) but the raffinose was hydrated ($C_{18}H_{32}O_{16}.5H_2O$).

The solutions were diffused in the column, samples being withdrawn at frequent intervals and analysed by the refractometer; the initial rates were then obtained graphically as already described, for glucose, and converted into S-values as usual.

Results.

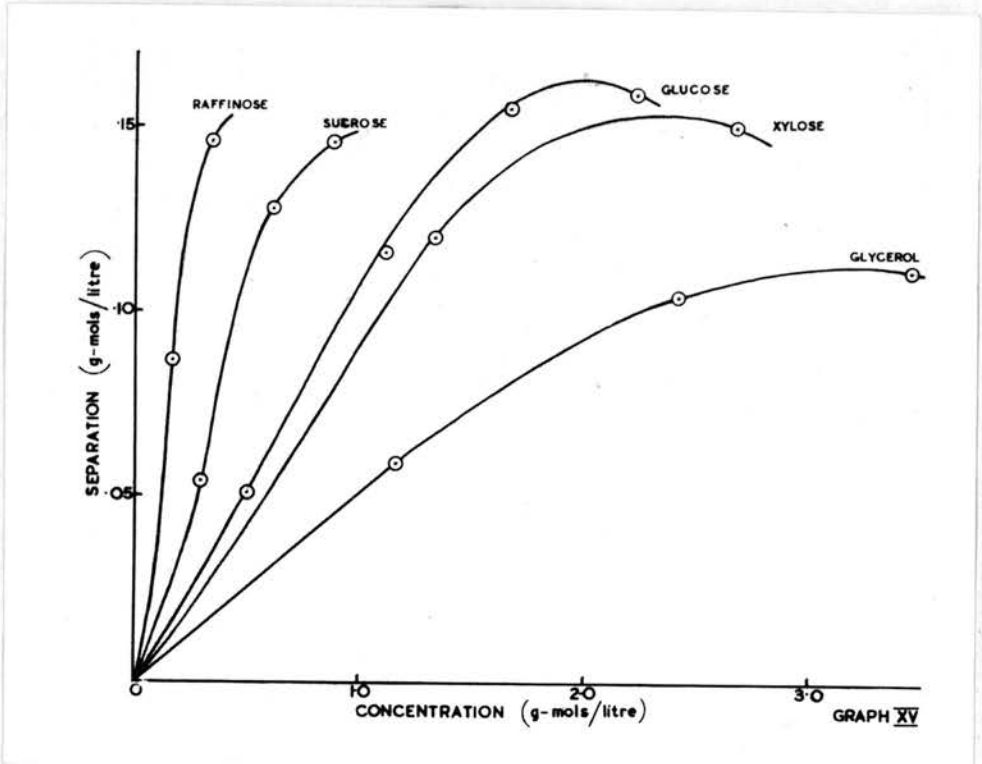
Solute	x_i Initial [Solute] (g-mol/litre)	Δx_i [Solute] increase (g-mol/litre/min.)	Initial Rate S^{obs}
Xylose	1.332	0.013	0.12
"	2.665	0.016	0.15
Raffinose	0.168	0.003	0.09
"	0.337	0.005	0.15

These figures are now incorporated in Graph XV together with the corresponding data for Glycerol, Glucose and Sucrose. In order to avoid the crossing over /

over of Graphs the values for glucose and sucrose at higher concentrations have been omitted.

Viscosity data for Xylose and Raffinose are either incomplete or not available; the initial rates have thus not been treated as in previous sections and are presented purely as experimental results.

Comparing the various curves, it is seen that at low concentrations, the initial rate increases with increasing molecular weight of the solute. The turn-over at higher concentrations is, of course, largely due to increase in viscosity which reduces the speed of convection, as described in the theoretical section.



GRAPH XV

Experiments using the Soret Effect.

It was assumed that the rate of convective thermal diffusion was equal to the rate of simple thermal diffusion multiplied by the rate of the convection, and this was taken to be justified on the ground that the formula based on it, accurately predicted the temperature dependence of the separation.

It was considered, however, that it would be interesting to attempt to verify this assumption directly by measuring both the simple Soret separation and the convected separation in the column and thus finding out if the two were correctly related to each other by the convection formula.

For this purpose a minimum of two solutes was required, both giving large enough Soret effects to be measured in a reasonably short time. Investigation of the literature showed that hydrochloric and sulphuric acids were suitable; they were also convenient due to the ease of their volumetric estimation. Accordingly, normal solutions (for which a maximum separation of hydrochloric acid was obtained by Chipman[7]) of both acids were subjected to a temperature gradient established between steam (100°C.) and cold water (5°C.) in the straight Soret Tube A (described in the experimental section) for a period of 7 hours.

Results /

Results.

Solute	Original [Acid] g-mol/l.	Final [Acid] g-mol/litre Upper	Centre	Lower	[Acid] increase in Lower portion
HCl	1.120	1.068	1.120	1.168	0.048
H_2SO_4	0.520	0.510	0.520	0.535	0.015

It will be noted that it is the separation at the foot of the Soret tube which is considered; this corresponds to the separation at the foot of the column with which it will be compared shortly.

The figures in the last column are taken to give relative values of the initial rate of the Soret separation. In order to calculate relative initial rates of the convected separation from these figures we require values for the convection. For constant temperature conditions these are given by $v = \frac{\rho}{\eta}$ where ρ is the density of the solution and η is its viscosity at the mean temperature of the column. Since the only figures available are at 25°C., these have been used on the assumption that little relative variation will occur between 25°C. and 50°C. - which is probably justified since the solutions are so dilute. We now form

$$S^{CALC} = \frac{\rho}{\eta} \times [\text{ACID}]_{\text{INCREASE}}$$

which may be expected to give relative values of the convected separation.

Solute /

Solute	ρ	η_{25}	S^{CALC}
HCl	1.007	9.49	0.005100
H_2SO_4	1.019	9.76	0.001566

The determination of the convective separation presented some difficulty since the separation was so rapid that the time of withdrawal was very critical. For this reason equilibrium separations were measured instead. This may seem rather arbitrary, but it may be shown that it is justified. For the dilute (c. 5%) solutions used both the initial rate and the equilibrium separations are linear functions of the original concentration and so bear a constant ratio to each other. It was found that equilibrium was reached in 7 hours, in striking contrast to the results with non-electrolytes.

Results.

Solute	Original [Acid] g-mol/litre	Final [Acid] g-mol/litre	S^{OBS} = [Acid] increase g-mol/litre	$\frac{S^{OBS}}{S^{CALC}}$
HCl	1.120	3.050	1.930	378
H_2SO_4	0.520	1.140	0.620	396

The results are seen to agree fairly closely; it is now realised that a more severe test would have been to use solutions whose viscosities were less similar. However, since this was considered to demonstrate that the principle is essentially correct, the matter was not /

not pursued further.

An attempt was also made to measure the velocity of the convection directly. For this purpose the diffusion column was placed in a glass outer jacket and filled with normal hydrochloric acid, and to the acid at the foot only was added a few drops of methyl red. The water cooling and steam heating were then turned on and the red colour passed up the tube, but in so doing it got fainter and fainter on account of dilution. It was considered, however, that the red colour was first detectable at the top of the column in 2 minutes. It is seen then that the convection current is fairly rapid. The experiment was also repeated adding the indicator at the top in case the alcohol in which the indicator was dissolved had accelerated its passage to the top of the column. In this case also the red colour could be detected at the foot in about 2 minutes. No great accuracy is possible by the present method, and the figures are not considered suitable for calculation. Although there was no sign of the indicator concentrating at the top or the foot, it is realised that it is the speed of movement of the solute studied which is desired and not that of an indicator. A suitable method would be the use of a radio-active isotope with Geiger counters at top and foot.

Further Theoretical Treatment - Gases.

In the discussion of the thermal diffusion of liquids it was indicated that further development of the theory was handicapped by the lack of knowledge concerning the diffusion diameter of the various molecules concerned. In the case of gases, however, due to our greater knowledge of the conditions prevailing in the gaseous state, a more detailed discussion is possible. This is now given: for, although no experimental work has been done with gases in the present investigation, it is considered very much to the point to compare the gas equation with the published experimental results and also with the other equations which have been derived; and for this reason, that the model on which the gas and liquid equations have been built is essentially the same, and support for one equation is incidentally support for the other.

The equation obtained for the initial separation was

$$S = \frac{x_1 x_2}{x_1 + x_2}\left(D^{x_1}_{x_1 x_2} - D^{x_2}_{x_1 x_2}\right)\log T \qquad \ldots\ldots\ldots (1)$$

where $$D^{x_1}_{x_1 x_2} \propto \left[\frac{\sigma^2_{1.1}}{\sqrt{\frac{1}{M_1}+\frac{1}{M_1}}} + \frac{\sigma^2_{1.2}}{\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}}\right]^{-1} \qquad \ldots\ldots\ldots\ldots (2)$$

and /

and $D^{x_2}_{x_1 x_2}$ similarly: x_1 and x_2 are the concentrations of the gases of molecular weight M_1 and M_2, and the σ's are collisional diameters. It is usual also to put

$$D_T = \frac{x_1 x_2}{x_1 + x_2}\left(D^{x_1}_{x_1 x_2} - D^{x_2}_{x_1 x_2}\right) \qquad \ldots\ldots\ldots\ldots\ldots (3)$$

Examination of equation (1) reveals that for given diameters and masses the sign of the separation is always +ve or -ve or zero independent of the relative concentrations; for a particular binary mixture, there is no indication of a change in sign as the relative concentrations are altered. To explain such a change as experimentally observed by Grew[42] for mixtures of neon and ammonia, it is thus necessary to recognise the fact that the above simple equations (1) and (2) are inadequate and a factor must be introduced which does alter with concentration. This may be identified with the interaction of molecule on molecule and may be expressed by means of a force law, which is not indicated by elementary kinetic theory.

Force Law Correction. (i) Case of Ammonia and Neon.

The sign of the separation depends on the difference between the two diffusion coefficients $D^{x_1}_{x_1 x_2}$ and $D^{x_2}_{x_1 x_2}$: when this difference is small, i.e., when mass and diameter effects are approximately equal, any departure /

departure from 'ideal' conditions will have a relatively large effect. In the neon-ammonia separation quoted we may take neon (on compressibility grounds) to approximate more closely to ideal gas law conditions: the diffusion of a neon molecule through different pressures of neon gas will then be approximately according to the above law. Similarly for the diffusion of a neon molecule through different pressures of ammonia, we may assume more or less negligible departure from ideal conditions for the $Ne - NH_3$ collision. On the other hand, while the ammonia molecule will conversely diffuse through different neon pressures with unaltered $\sigma_{NH_3\text{-}Ne}$ $\left(= \sigma_{Ne\text{-}NH_3}\right)$, for mixtures containing increasing pressures of ammonia, the rate of diffusion will be smaller than the ideal rate, because of the "softness" of the NH_3 molecules: thus the effective radius $\frac{1}{2}\sigma$ NH_3-NH_3 will be greater than the corresponding radius in the NH_3-Ne collision. The equation may then be corrected by the addition of the factor $1+\lambda$ so that for $X_1 = NH_3$, $X_2 = Ne$:-

$$D^{X_1}_{X_1X_2} \propto \left[\frac{X_1(1+\lambda)\sigma_{1\cdot1}^2}{\sqrt{\frac{1}{M_1}+\frac{1}{M_1}}} + \frac{X_2\sigma_{1\cdot2}^2}{\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}} \right]^{-1}$$

and $$D^{X_2}_{X_1X_2} \propto \left[\frac{X_1\sigma_{2\cdot1}^2}{\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}} + \frac{X_2\sigma_{2\cdot2}^2}{\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}} \right]^{-1}$$

For /

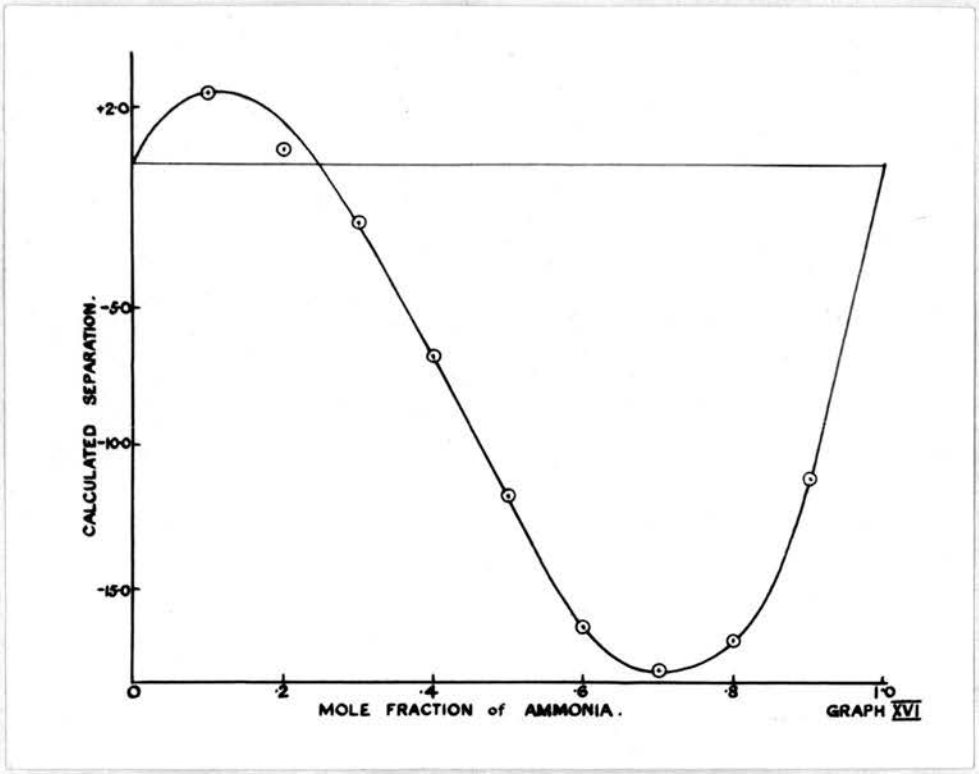
For certain relative values of σ, values of $1+\lambda$ which are not far removed from unity, are sufficient to predict a change in sign as x_1/x_2 is altered. If for example $1+\lambda = 1{\cdot}03$,

$NH_3 = M_1 = 17$, $Ne = M_2 = 20$,

$\sigma_{1.1} = 2{\cdot}38$, $\sigma_{2.2} = 2{\cdot}30$, $\sigma_{1.2} = \sigma_{2.1} = 2{\cdot}34$

x_1	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	
x_2	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0	
D_T $(\times 10^5)$	0.0	2.52	0.48	-2.10	-6.72	-11.75	-16.32	-17.85	-16.8	-11.6	0.0	

For concentrations of ammonia up to 25%, D_T is $+\varkappa$, which corresponds to normal thermal diffusion, the heavier neon molecule concentrating at the foot of the column. Above 25%, D_T is $-\varkappa$, which corresponds to the heavier neon molecule concentrating at the top of the column. These calculations are in agreement with the result of Grew (loc.cit.). In Graph XVI the calculated values are plotted against neon concentrations: if the experimental separations obtained by Grew are also plotted with suitable co-ordinates good agreement is obtained.


+2·0
-50
-100
-150
CALCULATED SEPARATION.
0
·2
·4
·6
·8
1·0
MOLE FRACTION of AMMONIA.

GRAPH XVI

It is, of course, realised, and must be emphasised, that the above treatment is a very much simplified approach to a very complex problem.

Force Law Correction. (ii) General Case.

In the above discussion it has been indicated that while the simple equation (1) gives some idea of thermal diffusion factors it will not accurately account for the observed phenomena in actual molecules. A $1+\lambda$ factor would then be required for each of the collisions $M_1 - M_1$, $M_1 - M_2$, and $M_2 - M_2$ and the effect of such factors may then greatly alter the application of the simple formula, and since it involves the square of the diameter and only the square root of the mass, any change in the effective diameter will have a relatively large effect. Thermal diffusion with actual molecules cannot therefore be dealt with strictly on the simple (rigid-elastic-sphere) kinetic theory basis above, but must be largely dependent on the force law governing the approach of molecules.

An indication of the effect of such a force law may be presented as follows. The above theory is based on the assumption that the rate of diffusion on the high temperature side is greater than that on the low temperature side solely because of the decrease in concentration of particles at the higher temperature.

More /

More correctly, the rate of diffusion will be determined by the collision rate of the diffusing molecule, and, in particular, if the number of collisions per. sec. is the same in both temperature regions no thermal diffusion will occur, no matter what the concentration may be. Accordingly we proceed to evaluate an expression for the number of collisions per second (per unit volume).

The number of collisions per second will be proportional to the effective collision area and to the velocity of the molecule only (since the pressure is assumed to remain constant - cf. Glasstone[69] p.269), i.e., $Z \propto V\sigma^2$ where $V=(c^{-2})^{\frac{1}{2}}$ as usual.

Now let the repulsive force between the molecules be represented by $F = \frac{-K}{r^s}$ where r is the distance between the molecules: then following Frankel[28], we may derive $V\sigma^2$ in terms of V only by the dimensioned method.

Since $\frac{K}{r^s}$ has the dimensions of a force (MLT^{-2}), K has dimensions $(ML^{s+1}T^{-2})$. Now mV^2 is of dimensions (ML^2T^{-2}) so that $\frac{K}{mV^2}$ is of dimensions (L^{s-1})

The radius σ, being of dimensions L, must then be proportional to $\left(\frac{K}{mV^2}\right)^{\frac{1}{s-1}}$ or to $V^{\frac{-2}{s-1}}$

for constant m and K. Hence the number of collisions is proportional to $V.V^{\frac{-4}{s-1}} = V^{\frac{s-5}{s-1}}$.

Now /

Now the velocity V will increase with temperature and will thus be greater on the high temperature side. If however, $s=5$ ("Maxwellian" molecules), the number of collisions per second will be constant for each side being proportional to unity (V^0); in other words thermal diffusion will not be observed.

If $s>5$ the number of collisions will be greater on the high temperature side corresponding to a greater V: in other words, on account of the constant pressure conditions, the diffusing molecule will move further on the hot side than on the cold. This is the state of affairs corresponding to the elementary theory above; high values of s then tend to approximate to kinetic theory conditions.

If $s<5$ the number of collisions will be proportional to V to a -ve power, i.e., $\propto \frac{1}{V^x}$, say, and with V increasing with increasing rise of temperature, this corresponds to the diffusing molecule moving farther on the cold side than the hot. This corresponds to the case of CO_2-cyclopropane[38] or of neon-ammonia mixtures in which the ammonia concentration exceeds 0.25 mole fraction.

It is thus clear that the above simple theory cannot be directly applied to all gaseous mixtures because of the force law.

Force /

Force Law Correction. (iii) Case of Isotopes.

In the case of two isotopes, however, while the masses are different the diameter and force law corrections may be taken as the same for each species. The numerical value of the D_T factor will depend on the unknown effective diameter, but the ratio k_T of this factor to the coefficient D of ordinary diffusion will not contain a diameter term, and may thus be compared with the value derived from more rigorous theory.

With $x_1 + x_2 = 1$ so that x_1 and x_2 are the respective relative concentrations, and the ratio of the isotopic masses not far removed from unity, the coefficient of ordinary diffusion may be taken as

$$D = \frac{\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{\sigma^2 (x_1 + x_2)}$$

The ratio k_T may then be simplified to

$$k_T = \frac{D_T}{D} = x_1 x_2 \left[\left(x_2 + \frac{x_1}{\sqrt{2}} \sqrt{1 + \frac{M_1}{M_2}} \right)^{-1} - \left(x_1 + \frac{x_2}{\sqrt{2}} \sqrt{1 + \frac{M_2}{M_1}} \right)^{-1} \right] \cdots \quad \cdots\cdots (4)$$

Furry, Jones and Onsager[37] quote Enskog's result for this particular case as

$$k_T = \frac{105}{18} \cdot \frac{M_2 - M_1}{M_2 + M_1} \cdot x_1 x_2 \quad \cdots\cdots\cdots\cdots (5)$$

and Chapman's earlier expression as

$$k_T = \frac{14}{3} \cdot \frac{M_2 - M_1}{M_2 + M_1} \cdot \frac{x_1 x_2}{(9.15 - 8.25 x_1 x_2)} \quad \cdots\cdots\cdots (6)$$

Comparison of these expressions is best shown by a numerical example. With $M_1 = 100$, $M_2 = 110$, results are given in the following table under the headings (4), (5), and (6) respectively.

Table of k_T values $M_1 = 100$, $M_2 = 110$.

x_1	(4)	(5)	(6)	(7)
0.1	0.0024	0.0038	0.0029	0.0015
0.5	0.0060	0.0106	0.0095	0.0042
0.9	0.0023	0.0038	0.0029	0.0015

Experimental determinations of k_T for the case of dissimilar molecules lead Furry Jones and Onsager to suggest that

$$k_T = 0.35 \frac{M_2 - M_1}{M_2 + M_1} \cdot x_1 x_2 \qquad \ldots\ldots\ldots\ldots (7)$$

be used as a provisional value for the design of apparatus. These values are also included in the above table.

It is to be noted therefore that formula (4) above may therefore be employed to give reasonable values of the k_T ratio.

Case of a Ternary Gaseous Mixture.

One advantage of the present representation lies in the relatively simple calculation of the effect of a /

a third gas on the two-constituent separation. This may be achieved as follows.

The time taken for one "A" molecule to diffuse through X_1 molecules at concentration x_1, plus X_2 molecules at concentration x_2, plus X_3 molecules at concentration x_3, will be the sum of the times taken to diffuse through each separately.

$$\text{i.e.} \quad \frac{1}{D^A_{x_1x_2x_3}} = \frac{x_1}{D^A_{x_1}} + \frac{x_2}{D^A_{x_2}} + \frac{x_3}{D^A_{x_3}}$$

The derivation thereafter continues just as before.

Calculation then shows that the addition of a small amount of a light gas such as hydrogen might be expected to facilitate greatly the separation of gases of similar molecular weight or of isotopes. This is in agreement with the conclusion reached by Gillespie[26] on the basis of more rigorous theory.

Summary /

Summary

Thermal Diffusion in some aqueous solutions has been studied by means of a Clusius & Dickel convection column of the concentric cylinder type, made from soft glass (height 1.28 metres, radial gap 0.68 mm.).

The property measured in all but a few cases was the initial rate of the separation of solute from solvent - a new departure in this field.

Most attention was given to Glycerol, Glucose and Sucrose, and for these solutes the variation of the initial rate with concentration and with temperature was studied. Acetone, xylose, raffinose, hydrochloric acid and sulphuric acid were also studied but to a less extent.

A new approach to the theory of simple Thermal Diffusion in gases was used to obtain an equation which was demonstrated, by comparison with experimental results and with more rigorous theory, to be correct in its essentials.

A similar model was then used to derive an equation for the initial rate in the liquid state and in the convection column. This equation was:-

$$S = \frac{\beta\rho\Delta T}{\eta_T} \cdot \frac{x_1 x_2 (V_1+V_2)}{(V_1 x_1 + V_2 x_2)} \left(\frac{T_2}{\eta_2} - \frac{T_1}{\eta_1}\right)\left(\frac{1}{\alpha_2} - \frac{1}{\alpha_1}\right)$$

where /

where x_1, V_1 and α_1 are the concentration, molecular volume and molecular "diffusion" diameter of the solute and x_2, V_2 and α_2 refer to the solvent (water). η_2, η_1 and $\eta_{\bar{T}}$ refer to the viscosity of the solution employed at the hot wall (temperature T_2), the cold wall (temperature T_1), and at the mean temperature of the column $\bar{T}$ $\left[\bar{T} = \frac{1}{2}(T_1 + T_2)\right]$. ρ is the density of the solution at 20°C. and β is its coefficient of cubical expansion. $\Delta T = T_2 - T_1$.

This equation predicts that with increasing concentration the initial rate should increase, pass through a maximum and subsequently decrease. With this, the experimental results are in general agreement. Further, the rather complicated changes in the initial rate, which are observed experimentally as the mean temperature, $\bar{T}$, and the temperature difference, ΔT, are varied, are closely reproduced by this equation.

It is indicated that the term which is most difficult to evaluate is $\left(\frac{1}{\alpha_2} - \frac{1}{\alpha_1}\right)$. The method of calculation used, which is based on molar volumes, fails to account, for example, for the fact that acetone alone of all the solutes studied, diffuses to the hot wall and thence to the top of the column. The conclusion is reached that this method of calculation of diffusional diameters is not sufficiently accurate for the purpose.

Some /

Some experiments have been carried out with two solutes in the same solution, and small relative separations recorded. A few determinations of equilibrium separations have been carried out with concentrated sucrose solutions. Two non-convective Soret experiments were carried out with dilute hydrochloric and sulphuric acids respectively.

Finally, the ready adaptation of the simple gas theory, to explain some of the more complex phenomena which are observed, has been demonstrated.

Finally the author wishes to thank his supervisor, Dr Mowbray Ritchie, for the constant advice, encouragement and assistance which he has given in the course of this work, and Professor James Kendall for some useful suggestions and a great deal of less direct assistance.

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